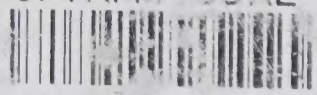




CFTRI-MYSORE



Structure and co

THE
STRUCTURE AND COMPOSITION
OF FOODS

THE STRUCTURE AND COMPOSITION OF FOODS

BY

ANDREW L. WINTON

AND

KATE BARBER WINTON

VOLUME I

Cereals, Starch, Oil Seeds, Nuts, Oils, Forage Plants
710 pages, 274 illustrations

VOLUME II

Vegetables, Legumes, Fruits
904 pages, 303 illustrations

VOLUME III

Milk (including Human), Butter, Cheese,
Ice Cream, Eggs, Meat, Meat Extracts, Gelatin,
Animal Fats, Poultry, Fish, Shellfish
524 pages, illustrated

VOLUME IV

Sugar, Sirup, Honey, Tea, Coffee, Cocoa, Spices,
Extracts, Yeast, Baking Powder
580 pages, 134 illustrations

PUBLISHED BY

JOHN WILEY & SONS, Inc.

THE STRUCTURE AND COMPOSITION OF FOODS

BY

ANDREW L. WINTON, PH.D.

Sometime State and Federal Chemist

AND

KATE BARBER WINTON, PH.D.

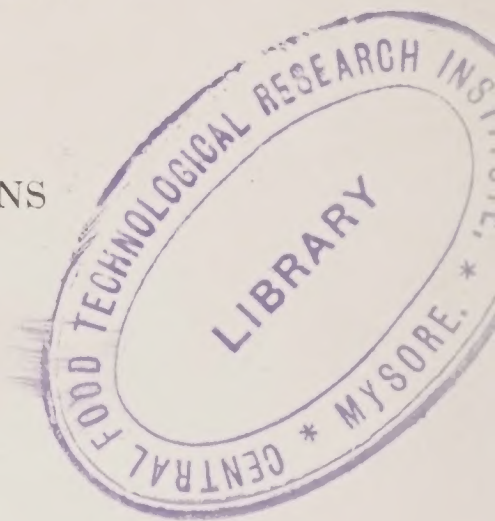
Sometime State and Federal Microscopist

VOLUME IV

SUGAR, SIRUP, HONEY, TEA, COFFEE, COCOA,
SPICES, EXTRACTS, YEAST,
BAKING POWDER

WITH 134 ILLUSTRATIONS

BY THE AUTHORS



NEW YORK

JOHN WILEY & SONS, INC.

LONDON: CHAPMAN & HALL, LIMITED

1939

705 ✓

COPYRIGHT, 1939

BY

ANDREW L. WINTON AND KATE BARBER WINTON

COPYRIGHTED, CANADA, 1939, INTERNATIONAL COPYRIGHT, 1939

ANDREW L. WINTON and KATE BARBER WINTON, *Proprietors*

All Rights Reserved

*This book or any part thereof must not
be reproduced in any form without
the written permission of the publisher.*

F8, 3; e

N 35.4

CFTRI-MYSORE



705

Structure and co.

PRINTED IN U. S. A.

PRESS OF
BRAUNWORTH & CO., INC.
BUILDERS OF BOOKS
BRIDGEPORT, CONN.

PREFACE

Of the four parts into which this, the last volume of the series, is divided, only Part I, on sugar, sirup, and other saccharine products, is devoted to foods in the strict sense, that is, foods consisting essentially of nutritive constituents. The remaining three parts deal with food adjuncts, that is, materials which serve to impart to true foods desirable properties such as stimulation, flavor, or mechanical condition. So-called alkaloidal foods, considered in Part II, are remarkable from the chemical viewpoint because the active constituents belong to the purine group, thus showing a relationship to the extractive matters of meat. Psychologically the association of these purines with desirable flavors is remarkable. The spices and other flavoring materials, dealt with in Part III, owe their value chiefly to terpenes which form another absorbing group. Compounds of still other organic groups add further interest. Lastly, Part IV, on leaven, deals with materials of a radically different nature, namely, (1) the living yeast plant of minute size and of intricate constitution, which through fermentation causes the evolution of carbon dioxide in the loaf, and (2) baking powders which in a purely chemical way liberate carbon dioxide.

A diligent attempt has been made in the Addenda, as in the Introduction to Volume II and the Addenda to Volume III, to keep pace with the startling developments in vitamin chemistry, especially the framing of structural formulas of the individual vitamins. It remains by suitable analytical methods, some already in practical use, to determine these vitamins quantitatively in the numerous natural food products and to locate them in the tissues by suitable tests.

The various fruits, seeds, leaves, rhizomes, and barks treated in Parts II and III, also the pollen grains of honey (Part I) and the cells of the yeast plant (Part IV), under the microscope display a wide variety of characteristic forms and permit the application of various microchemical tests. In these products the relation of structure to composition is particularly intimate.

Supplementing a statement in the Introduction to Volume I, the authors urge recognition of food histology as the logical, although

more, approach of the student to food science and of the trained chemist to food research of a more fundamental character than the mere diagnosis of commercial doubts and unknowns, in which field the authors long labored. Proximate analyses are cold aggregates of figures, often failing to differentiate radically unlike substances, but when these figures are considered in conjunction with botanical classification and the marvelous cell forms and cell contents, the various cereals, vegetables, fruits, alkaloids, and spices stand out as illuminated structures in which each constituent has "a local habitation and a name."

A. L. W.

K. B. W.

WILTON, CONN.

October, 1938

ACKNOWLEDGMENTS

Information on the technology and chemistry of sugars and other saccharine products was generously furnished by Dr. C. A. Browne and Dr. C. S. Hudson of Washington, D. C., and Dr. W. D. Horne of Beech Creek, Pa.

A supply of coffee beans before shelling was obtained through the courtesy of Arbuckle Brothers of New York. Representative samples of cocoa beans from different countries, invaluable for comparison, were contributed by Walter Baker & Co. of Dorchester, Mass., and Scarborough Company of New York. A tribute is due the late Mr. Clifford Langley for assistance during his association with the senior author in official work and subsequently during his association with Huyler's.

From time to time during over forty years, several houses, recognized as leading importers of spices, were ever ready to furnish information and authentic material. Among these houses, some no longer in business, were D. & L. Slade Co. and Stickney & Poor, Boston; E. R. Durkee & Co., Francis H. Leggett & Co., and Austin, Nichols & Co., New York; Bennett, Simpson & Co., London and New York; The A. Colburn Co., Philadelphia; The Thompson & Taylor Spice Co., Chicago; McCormick & Company, Baltimore; and R. T. French Co., Rochester, N. Y.

Vanilla and tonka beans from widely separated regions were obtained from M. L. Barrett & Co., Chicago, Ill.

The Fleischmann Laboratories kindly furnished samples of different types of yeast.

Pleasant memories, extending back over fifty years, are revived by crediting in various parts of the text former associates with their part in special investigations, the results of which were published originally in official documents or scientific journals.

CONTENTS

PART I

SACCHARINE PRODUCTS

	PAGE
SACCHARINE PRODUCTS	1
Introduction	1
Physical Properties of Sugars	2
Crystallization	2
Solubility	3
Sweetness	3
Polarization	3
Chemical Constitution of Sugars	4
Chemical Reactions	9
Sugar Cane Products	10
Manufacture of Crude Sugar	10
Sugar Refining	12
Chemical Composition	12
Sugar	16
Molasses	19
Cane Sugar Sirup	21
Constituents	21
Proteins	21
Amino Acids	21
Purine Bases	22
Choline Bases	22
Amides	22
Acids	22
Carbohydrates	23
Colors	23
Mineral Constituents	23
Minor Mineral Constituents	24
Sorghum Products	25
Sorghum Sirup	25
Corn Stalk Products	27
Palm Stalk Products	28
Nipa Palm Sugar	28
Date Palm Sugar	28
Sugar Palm Sugar	28
Palmyra Palm Sugar	28
Sugar Beet Products	29
Manufacture of Beet Sugar	29
Microscopic Structure	29
Chemical Composition	30
Juice	30

	PAGE
Raw Sugar	30
Refined Sugar	31
Molasses	31
Constituents	32
Proteins	32
Amino Acids	32
Choline Base	32
Nitrates	32
Acids	33
Carbohydrates	33
Colors	34
Mineral Constituents	34
Maple Products	36
Maple Sap	36
Manufacture of Maple Sirup and Maple Sugar	36
Statistics of Production	36
Definitions and Standards	37
Chemical Composition	37
Constituents	41
Acids	41
Carbohydrates	42
Colors	42
Flavor	42
Various Constituents	43
Enzymes	43
Bacteria	43
Mineral Constituents	43
Minor Mineral Constituents	44
Honey	45
Standard Honey	45
Fermentation of Floral Honey	45
Honeydew Honey	46
Noor Honey	46
Feeding Sugar Sirup	47
Fermentation of Honey	47
Adulteration	47
Microscopic Structure	48
Pollen	48
Physical Characters	49
Flavor	49
Color	51
Granulation	51
Polarization	51
Chemical Composition	52
Influence of Age	58
Constituents	58
Proteins	58
Tannin	59
Acids	59
Carbohydrates	60

CONTENTS

xi

	PAGE
Enzymes	63
Flavor	65
Colors	65
Fluorescence in Ultra-Violet Light	65
Mineral Constituents	65
Minor Mineral Constituents	66
Invert Sugar Sirup	67
Artificial Honey	68
Tests for Invert Sugar Sirup	69
Starch Sugar and Glucose	72
Process of Manufacture	72
Uses	73
Chemical Composition	73
Commercial Glucose	73
Maize vs. Potato Glucoses	74
Various Products	75
Malt Sirup	75
Carob Bean Sugar and Molasses	75
Grape-vine Sirup	75
Caramel	76
Uses	76
Chemical Composition	76
Minor Constituents	77

PART II

ALKALOIDAL PRODUCTS

ALKALOIDAL PRODUCTS	81
Introduction	81
Chemical Constituents	81
Purine Bases	81
Pyrimidine Bases	84
LEAVES OF THE COCA FAMILY (<i>Erythroxylaceæ</i>)	85
Coca Leaf (<i>Erythroxylon Coca</i>)	85
LEAVES OF THE HOLLY FAMILY (<i>Acquisfoliaceæ</i>)	87
Maté (<i>Ilex paraguariensis</i>)	87
LEAVES OF THE TEA FAMILY (<i>Ternstraëmiaceæ</i>)	94
Tea (<i>Thea sinensis</i>)	94
Macroscopic Structure	95
Microscopic Structure	96
Chemical Composition	97
Influence of Maturity on Composition	99
Influence of Method of Curing on Composition	100
Influence of Rolling on Solubility	100
Influence of Firing on Quality and Composition	101
Stems	101
Constituents	102
Proteins	102
Purine Bases	102
Fixed Oil	103

	PAGE
Volatile Oil	104
Oxalic Acid	105
Ascorbic Acid	105
Tannin	105
Saponin	108
Colors	109
Odor	109
Enzymes	109
Mineral Constituents	109
SEEDS OF THE PALM FAMILY (<i>Palmaceæ</i>)	112
Betel Nut (<i>Areca Catechu</i>)	112
SEEDS OF THE SOAPBERRY FAMILY (<i>Sapindaceæ</i>)	113
Guarana (<i>Paullinia Cupana</i>)	113
SEEDS OF THE STERCULIA FAMILY (<i>Sterculiaceæ</i>)	114
Chocolate and Cocoa	114
Cocoa (<i>Theobroma Cacao</i>)	114
Macroscopic Structure	115
Microscopic Structure	116
Chemical Composition	119
Cocoa Nibs and Shells	119
Effects of Roasting on Composition	120
Commercial Cocoa and Chocolate	120
Germ	125
Changes During Fermentation	126
Milk Chocolate	126
Compounds of Chocolate and Cocoa	127
Constituents	127
Proteins	127
Purine Bases	128
Other Nitrogenous Compounds	128
Fat	128
Volatile Oil	131
Organic Acids	132
Carbohydrates	133
Colors	133
Phosphorus-Organic Compounds	135
Mineral Constituents	135
Cola Nut (<i>Cola</i> spp.)	137
SEEDS OF THE MIMOSA FAMILY (<i>Rubiaceæ</i>)	139
Coffee (<i>Coffea arabica</i>)	140
Decortication	141
Roasting	141
Grinding	141
Preparation of Beverage	141
Caffeine-Free Coffee	142
Tannin-Free Coffee	142
Vacuum-Packed Coffee	142
Coffee Extracts	142
Chicory	142
Substitutes	142

CONTENTS

xiii

	PAGE
Macroscopic Structure	144
Varieties	145
Microscopic Structure	145
Chemical Composition	147
Influence of Roasting on Composition	147
Staling of Coffee and Vacuum Packing	150
Caffeine-Free Coffee	153
Tannin-Free Coffee	153
Coffee Extracts	154
Coffee Substitutes	154
Constituents	154
Purine Bases	154
Choline Bases	155
Other Nitrogenous Substances	155
Fixed Oil	156
Volatile Oil	158
Organic Acids	158
Carbohydrates	160
Colors	161
Enzymes	161
Mineral Constituents	161
SEEDS OF THE PEA FAMILY (<i>Leguminosæ</i>)	163
Coffee Cassia (<i>Cassia occidentalis</i>)	163
ROOTS OF THE COMPOSITE FAMILY (<i>Compositæ</i>)	167
Chicory Root (<i>Cichorium Intybus</i>)	167
Dandelion Root (<i>Taraxicum officinale</i>)	173

PART III

SPICES AND EXTRACTS

SPICES AND EXTRACTS	177
Introduction	177
Chemical Constituents	178
Fixed Oil	178
Volatile Oil	179
Water-Soluble Flavoring Principles	183
Inert Organic Constituents	183
Formulas	184
STEM AND LEAF SPICES	187
Leaves of the Grass Family (<i>Gramineæ</i>)	187
Lemon Grass (<i>Cymbopogon citratus</i>)	187
Citronella (<i>Cymbopogon Nardus</i>)	189
Rhizomes of the Arum Family (<i>Araceæ</i>)	191
Calamus (<i>Acorus Calamus</i>)	191
Rhizomes of the Iris Family (<i>Iridaceæ</i>)	196
Orris (<i>Iris florentina</i>)	196
Rhizomes of the Ginger Family (<i>Zingiberaceæ</i>)	198
Ginger (<i>Zingiber officinale</i>)	198
Macroscopic Structure	199
Microscopic Structure	200

	PAGE
Chemical Composition	203
Fixed Oil	207
Volatile Oil	208
Pentosans	211
Turmeric (<i>Curcuma longa</i>)	211
Stems and Leaves of the Laurel Family (<i>Lauraceæ</i>)	215
Bay Leaf (<i>Laurus nobilis</i>)	215
Leaves of the Mint Family (<i>Labiataë</i>)	219
Sweet Basil (<i>Ocimum basilicum</i>)	221
Peppermint (<i>Mentha piperita</i>)	224
Macroscopic Structure	225
Microscopic Structure	225
Chemical Composition	226
Peppermint Oil	226
Terpeneless Peppermint Oil	230
Non-volatile Constituents	230
Japanese Peppermint (<i>Mentha arvensis</i> var. <i>piperascens</i>)	231
Water Mint (<i>Mentha aquatica</i>)	233
Spearmint (<i>Mentha spicata</i>)	234
Sweet Marjoram (<i>Origanum Majorana</i>)	236
Thyme (<i>Thymus vulgaris</i>)	240
Summer Savory (<i>Satureia hortensis</i>)	244
Rosemary (<i>Rosmarinus officinalis</i>)	246
Sage (<i>Salvia officinalis</i>)	249
Clary (<i>Salvia Sclarea</i>)	252
Stems and Leaves of the Composite Family (<i>Compositæ</i>)	255
Tarragon (<i>Artemisia Dracunculus</i>)	255
BARK SPICES	258
Barks of the Birch Family (<i>Betulaceæ</i>)	258
Birch (<i>Betula lenta</i>)	258
Barks of the Laurel Family (<i>Lauraceæ</i>)	260
China Cassia (<i>Cinnamomum Cassia</i>)	261
Macroscopic Structure	261
Microscopic Structure	261
Chemical Composition	263
Fixed Oil	263
Volatile Oil	265
Pentosans	267
Mineral Constituents	267
Batavia Cassia (<i>Cinnamomum Burmanni</i>)	269
Saigon Cassia (<i>Cinnamomum Loureirii</i>)	270
Ceylon Cinnamon (<i>Cinnamomum zeylanicum</i>)	271
Sassafras (<i>Sassafras variifolium</i>)	276
FLOWER SPICES	278
Flower Stigmas of the Iris Family (<i>Iridaceæ</i>)	278
Saffron (<i>Crocus sativus</i>)	278
Flowers of the Caper Family (<i>Capparidaceæ</i>)	283
Capers (<i>Capparis spinosa</i>)	283
Petals of the Rose Family (<i>Rosaceæ</i>)	287
Rose (<i>Rosa</i> spp.)	287

CONTENTS

XV

	PAGE
Flowers of the Violet Family (<i>Violaceæ</i>)	290
Violet (<i>Viola</i> spp.)	290
Flower Buds of the Myrtle Family (<i>Myrtaceæ</i>)	291
Cloves (<i>Eugenia aromatica</i>)	291
Macroscopic Structure	291
Microscopic Structure	292
Chemical Composition	295
Fixed Oil	295
Volatile Oil	297
Pentosans	299
Tannin	299
Mineral Constituents	300
FRUIT AND SEED SPICES	301
Fruits of the Pine Family (<i>Pinaceæ</i>)	301
Juniper Berry (<i>Juniperus communis</i>)	301
Fruits of the Ginger Family (<i>Zingiberaceæ</i>)	303
Cardamom (<i>Elettaria Cardamomum</i>)	303
Fruits of the Orchid Family (<i>Orchidaceæ</i>)	308
Vanilla (<i>Vanilla planifolia</i>)	308
Macroscopic Structure	309
Microscopic Structure	309
Chemical Composition	312
Vanilla Extract	312
Vanillin	316
Vanillic Acid	317
Heliotropin	318
Resins	318
Pentosans	318
Mineral Constituents	318
Fruits of the Pepper Family (<i>Piperaceæ</i>)	319
Pepper (<i>Piper nigrum</i>)	319
Macroscopic Structure	321
Microscopic Structure	322
Chemical Composition	327
Proteins	329
Alkaloids	331
Piperine	331
Fixed Oil	334
Volatile Oil	334
Acids	335
Carbohydrates	335
Mineral Constituents	336
Long Pepper (<i>Piper officinarium</i>)	336
Cubebs (<i>Piper Cubeba</i>)	339
Fruits of the Magnolia Family (<i>Magnoliaceæ</i>)	341
Star Anise (<i>Illicium verum</i>)	341
Seeds of the Nutmeg Family (<i>Myristicaceæ</i>)	345
Mace (<i>Myristica fragrans</i>)	345
Nutmeg (<i>Myristica fragrans</i>)	349
Macroscopic Structure	349

	PAGE
Microscopic Structure	349
Chemical Composition	351
Fixed Oil	351
Volatile Oil of Nutmeg and Mace	354
Myristicin	355
Carbohydrates	356
Colors	356
Fruits of the Laurel Family (<i>Lauraceæ</i>)	357
Cassia Buds (<i>Cinnamomum Cassia</i>)	357
Seeds of the Mustard Family (<i>Cruciferæ</i>)	361
Black Mustard (<i>Brassica nigra</i>)	363
Macroscopic Structure	363
Microscopic Structure	364
Chemical Composition	367
Proteins	368
Fixed Oil	368
Volatile Mustard Oil	369
Sinigrin	370
Carbohydrates	371
Phosphorus-Organic Compounds	371
Enzymes	371
Mineral Constituents	371
Sarepta or Brown Mustard (<i>Brassica Besseriæna</i>)	372
Indian Mustard (<i>Brassica juncea</i>)	374
Chinese Mustard (<i>Brassica juncea</i>)	377
White Mustard (<i>Brassica alba</i>)	378
Macroscopic Structure	378
Microscopic Structure	378
Chemical Composition	380
Proteins	380
Fixed Oil	380
Volatile Mustard Oil	381
Sinalbin	382
Sinalbin Mustard Oil	382
Sinapin	383
Sinapinic Acid	383
Carbohydrates	383
Phosphorus-Organic Compounds	383
Enzymes	383
Mineral Constituents	383
Charlock (<i>Brassica arvensis</i>)	384
Seeds of the Pea Family (<i>Leguminosæ</i>)	389
Fenugreek (<i>Trigonella Fœnum-Græcum</i>)	389
Tonka Bean (<i>Coumarouna odorata</i>)	394
Fruits of the Nasturtium Family (<i>Tropæolaceæ</i>)	398
Nasturtium (<i>Tropæolum majus</i>)	398
Fruits of the Rue Family (<i>Rutaceæ</i>)	399
Sweet Orange (<i>Citrus sinensis</i>)	399
Mandarin Orange and Tangerine (<i>Citrus nobilis</i>)	403
Lemon (<i>Citrus Limonia</i>)	403

CONTENTS

xvii

	PAGE
Lime (<i>Citrus aurantifolia</i>)	406
Grapefruit (<i>Citrus grandis</i>)	407
Fruits of the Myrtle Family (<i>Myrtaceæ</i>)	408
Allspice (<i>Pimenta officinalis</i>)	408
Fruits of the Parsley Family (<i>Umbelliferæ</i>)	414
Coriander (<i>Coriandrum sativum</i>)	416
Cumin (<i>Cuminum Cyminum</i>)	420
Dill (<i>Anethum graveolens</i>)	423
Fennel (<i>Fœniculum vulgare</i>)	426
Anise (<i>Pimpinella Anisum</i>)	430
Caraway (<i>Carum Carvi</i>)	434
Celery (<i>Apium graveolens</i>)	438
Parsley (<i>Petroselinum sativum</i>)	441
Fruits of the Nightshade Family (<i>Solanaceæ</i>)	443
Paprika (<i>Capsicum annuum</i>)	443
Macroscopic Structure	444
Microscopic Structure	444
Chemical Composition	447
Changes in Composition During Growth	449
Fixed Oil	450
Volatile Oil	451
Capsaicin	452
Acids	452
Carbohydrates	453
Colors	453
Mineral Constituents	454
Cayenne Pepper (<i>Capsicum frutescens</i>)	455
Capsicums (<i>Capsicum</i> spp.)	459

PART IV

LEAVEN

LEAVEN	465
Yeast	465
Manufacture	466
Vienna Process	466
Hayduck Process	466
Nitrogenous Yeast Foods	467
Storage	468
Nutritive Value of Yeasts	469
Yeast as Meat Substitute	469
Relation of Yeast to Mushrooms	470
Fermentation	470
Factors Influencing Fermentation	471
Gay-Lussac's Theory	471
Neuberg's Pyruvic Acid Theory	472
Kostytschev's Pyruvic Acid Theory	473
Schade's Formic Acid Theory	473
Palladin and Sabinin's Lactic Acid Theory	473
Harden and Young's Hexose Diphosphate Theory	473

	PAGE
Lebedev's Hexose Diphosphate Theories	475
Meyerhof's Hexose Diphosphate-Pyruvic Acid Theory	475
Microscopic Structure	477
Cell Forms	477
Staining	478
Chemical Composition	478
Influence of Yeast on Composition of Bread	479
Constituents of Yeast and Fermenting Mediums	479
Proteins	479
Free Amino Acids	483
Amines	483
Purine Bases	483
Pyrimidine Bases	483
Choline Bases	483
Chitin	483
Hydrocyanic Acid	483
Fat	483
Sterols	485
Acids	487
Alcohols	490
Aldehydes	491
Carbohydrates	492
Phosphorus-Organic Compounds	495
Sulphur-Organic Compounds	500
Colors and Related Substances	501
Enzymes and Coenzymes	505
Vitamins	520
Hormones	520
Bioses	521
Mineral Constituents	522
Minor Mineral Constituents	523
Baking Powder	524
Sodium Bicarbonate	525
Acid Constituents	525
Albumin	527
Classification and Reactions	527
Legal Rulings	529
INDEX	531

ADDENDA

VOLUMES II AND III

Vol. II, p. 17; Vol. III, p. xxi. **Vitamins.**—When the manuscript of Volume I was prepared, the vitamins were known only by their physiological action, not as chemical individuals; since that time, however, at least seven individual vitamins or groups have been isolated and formulated. These are A including its provitamin (carotene), B (B_1), C, D and E in several forms, G (riboflavin), and nicotinic acid, formerly classed under B. Others, especially B_6 , H, K, L, and P, are being intensively studied. Future progress will be more readily followed, since many of the stumbling blocks have now been removed and authors¹ of treatises on organic and physiological chemistry are concentrating on the chemistry of the different groups to which vitamins belong.

Vitamin A and Provitamin A (Carotene).—See also Volume II, pp. 9 and 17.

Unlike most vitamins, vitamin A, as isolated by Karrer, has no chemical name other than one fully descriptive which is unduly cumbersome. As noted below, at least two chemical substances are now known to have vitamin A potency, hence a single name will not be adequate.

Guilbert,² quoting Karrer and Schlientz³ and Smith and Milner,⁴ regards the content of carotene in forage plants, other than the beta-form, as negligible. No preformed vitamin A has been found in any plant source.

Holmes and Corbet⁵ prepared, by a freezing-out process, crystalline vitamin A from the unsaponifiable matter of ishinagi liver oil and other fish oils as isotropic, pale yellow needles, melting at 7.5 to

¹ Organic Chemistry, An Advanced Treatise (Edited by Gilman), with chapters by Johnson on pyrimidines, etc., by Bogert on carotenoids, by Wolfrom and by Raymond on carbohydrates, and by Strain on sterols, New York, 1938; Bodansky: Introduction to Physiological Chemistry, New York, 1938.

² Ind. Eng. Chem., Anal. Ed. 1934, **6**, 452.

³ Helv. Chim. Acta 1934, **17**, 7.

⁴ J. Biol. Chem. 1934, **104**, 437.

⁵ J. Am. Chem. Soc. 1937, **59**, 2042; Science 1937, **85**, 103.

8° C. and corresponding quite closely in composition to Karrer's formula (Volume II, p. 9).

Andersen and Levine¹ demonstrated that the Carr-Price method may be so conducted as to differentiate vitamin A from carotene. In a chloroform solution, antimony trichloride forms with carotene a blue color that remains unchanged at 60° C., whereas at that temperature with vitamin A a color develops varying from rose to wine red according to the dilution.

Gillam, Heilbron, Lederer, and Rosanova² and Gillam, Heilbron, Jones, and Lederer³ apply the designation *vitamin A₂* to a biologically active substance, present in liver oils of fresh-water fish, believed to differ from *vitamin A₁* in having one more double bond. It shows a spectroscopic absorption band at 345 m μ direct and one at 693 m μ with antimony trichloride in chloroform solution, whereas the corresponding bands for vitamin A₁, as found chiefly in the liver oils of mammals and salt-water fish, are 328 and 620 m μ respectively. Lederer and Rathmann,⁴ by spectroscopic analysis, classify European fishes in three groups, according to the E₆₉₃/E₆₂₀ value and the A₂/A₁ value (printed in bold face) of their liver oils, thus: (1) 1.9 to 2.6 and **5** pike-perch (*Lucioperca lucioperca* L.), pike (*Esox lucius* L.), and catfish (*Silurus glanis* L.); (2) 0.4 to 0.9 and **0.5**, trout (*Salmo trutta irideus*), sturgeon (*Acipenser sturio* L.), salmon (*Salmo solar* L.), and carp (*Cyprinus carpio* L.); and (3) below 0.3 and **0.1**, all marine fish and all marine and land mammals. Owing to overlapping of the bands, the band ratios are less than the vitamin ratios. Vitamin A₂ gave a second band with antimony trichloride in chloroform solution at 645 to 650 m μ which is evident when the other band is inhibited by the addition of the fat-acid fraction of the same oil.

Edisbury, Morton, and Simpkins,⁵ whose paper appeared in the same number of Nature as that of Gillam et al., describe a vitamin A₂, present in fresh-water fish liver, differing from the above in showing direct absorption bands at 350 and 287 m μ .

Vitamin B.—See also Volumes II, p. 19, and III, p. xxi.

The isolation, synthesis, structure, and uses of *thiamin* (B₁) are discussed by its discoverer Williams.⁶ In the form of a phosphoric

¹ Proc. Soc. Exptl. Biol. Med. 1935, **32**, 737.

² Nature 1937, **140**, 233.

³ Biochem. J. 1938, **32**, 405.

⁴ Compt. rend. 1938, **206**, 781.

⁵ Nature 1937, **140**, 234.

⁶ Ind. Eng. Chem. 1937, **29**, 980.

ester, it constitutes an essential part of an enzyme which is required for the utilization of carbohydrates.

Results by Robbins, Bartley, Hogan, and Richardson¹ are noteworthy, since they indicate that 2-methyl-5-bromomethyl-6-aminopyrimidine and 4-methyl-5- β -hydroxymethylthiazole, which may be regarded as representing the two parts of the thiamin molecule, fed together cure polyneuritis.

Imai² obtained, by the cleavage of oryzanin with sodium hydrogen sulphite, two products, (1) $C_6H_9N_3SO_3$ and (2) C_6H_9NOS . The first, believed to be methyl-2-methyl-6-aminopyrimidine-5-sulphonate, is practically insoluble in various solvents, but soluble in dilute alkali; the second, 4-methyl-5- β -hydroxyethylthiazole, identical with the substance obtained by Williams, is soluble in ether.

The chemical status of three factors, namely, *thiamin* (B_1), *riboflavin* (B_2 or G), and *nicotinic acid* (B_3), originally grouped under vitamin B, is now well established. The first of these is quite generally allowed the full claim to the name vitamin B; the second has for some time been known as vitamin G. Nicotinic acid, which does not appear to have a generally accepted alphabetic designation other than as a factor of B, is described below after vitamin G.

Swaminathan³ has devised a method for the determination of nicotinic acid depending on the yellow-green color produced by the pyrimidine ring when treated with cyanogen-bromine and aniline.

György⁴ announced results indicating that B_6 is the true pellagra preventive. Birch and György,⁵ who prepared B_6 by autolyzing wheat germ in water, suggest that it is basic and may contain a hydroxyl but not a primary amino group. György,⁶ starting with Peters' eluate,⁷ prepared crystalline vitamin B_6 with high antiscorbutic value, but without influence on growth.

Schultz and Matill⁸ recognize the factor B_6 , also the precipitate factor of Elvehjem, Koehn, and Oleson,⁹ but state that the filtrate factor of Elvehjem and Koehn¹⁰ is not essential for rats.

¹ Proc. Nat. Acad. Sci. U. S. 1937, **23**, 388.

² J. Biochem. (Japan) 1937, **25**, 95.

³ Nature 1938, **141**, 830.

⁴ Nature 1934, **133**, 498; Biochem. J. 1935, **29**, 741, 760.

⁵ Biochem. J. 1936, **30**, 304.

⁶ J. Am. Chem. Soc. 1938, **60**, 983.

⁷ Biochem. J. 1933, **27**, 225.

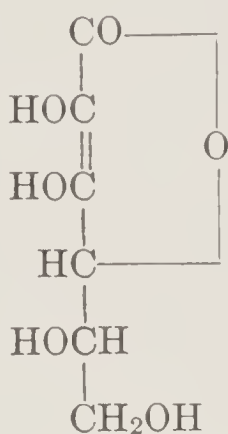
⁸ J. Biol. Chem. 1937, **122**, 183.

⁹ Ibid. 1936, **115**, 707.

¹⁰ Ibid. 1935, **108**, 709.

Keresztesy and Stevens¹ isolated vitamin B₆ as the hydrochloride melting at 204 to 206° C. Ultimate analysis corresponded to the following formula, C₈H₁₂NO₃Cl. The melting point of the base was 160° C. Its formula calculated from the ultimate composition is C₈H₁₁NO₃.

Vitamin C or l-Ascorbic Acid, C₆H₈O₆.—Of the two structural formulas given in Volume II, p. 21, the enolized form of the one credited to Haworth, given below, is now generally accepted. It forms reversibly dehydroascorbic acid by eliminating the hydrogens of the two hydroxyls in the ring.



Ascorbic Acid (Haworth, Hirst, et al.)

Haworth,² in whose laboratory the work was carried out, generously gives credit to Hirst and co-workers. Others whose names appear in two detailed papers³ are Herbert, Percival, Reynolds, Smith, Ault, Baird, Carrington, and Stacey. Although both the *d* and *l* forms were synthesized, it is the latter that corresponds with natural vitamin C in its physiological action. Ascorbic acid is not, as formerly thought, a true hexuronic acid, but may be designated as 3-keto-1-gulofuranolactone, an oxidation derivative of a sugar.

Giroud, Ratsimamanga, and Leblond⁴ observed that the green parts of plants are richer in ascorbic acid than the non-green parts.

Ascorbic acid was demonstrated histologically by Giroud and Leblond⁵ in the cytoplasm of animal cells, not in the nucleus, by its reaction with silver nitrate after vascular injection.

Pittarelli and Pittarelli⁶ found that the reducing action of copper

¹ Proc. Exp. Biol. & Med. 1938, **38**, 64; J. Am. Chem. Soc. 1938, **60**, 1267.

² Chem. & Ind. 1933, p. 482.

³ J. Chem. Sci. 1933, pp. 1270, 1419.

⁴ Compt. rend. soc. biol. 1934, **117**, 612.

⁵ Bul. histol. appl. physiol. path. tech. microscop. 1935, **12**, 49.

⁶ Policlinico, Sez. prat. 1935, p. 826.

sulphocyanate and mercurous chloride, unlike several reactions for ascorbic acid, is specific and rapid, thus permitting volumetric determination by titrating the excess.

Dischendorfer¹ demonstrates the presence of ascorbic acid in cell sap by the Prussian blue reaction, the brown coloration with potassium permanganate, and the red coloration with *o*-nitrosonitrobenzene. The blackening of chlorophyll grains with acid silver nitrate, caused by the liberation of the metal as discovered by Giroud, is also believed to be due to ascorbic acid.

Kohman and Sanborn² have shown that the juice of leguminous seeds contains *glutathione* and one or more other substances that reduce dehydroascorbic acid, thus protecting against oxidation of ascorbic acid in air. This reduction, also that of the oxidized glutathione and possibly other oxidized substances, is accelerated by enzymes. These substances introduce errors in the determination of ascorbic acid by titration with 2,6-dichlorophenolindophenol. Copper does not affect the reduction of dehydroascorbic acid by the reducing substances as it does the oxidation of ascorbic acid by oxygen.

Szent-Györgyi,³ answering Cox,⁴ calls attention to his lecture March 18, 1932,⁵ in which he gave experimental evidence that vitamin C is identical with hexuronic acid described by him in 1928.

Guha and Pal⁶ and Levy⁷ explain the increase in ascorbic acid on boiling cabbage and other vegetable foods as due to the liberation of the acid from its combination. Guha and Sen-Gupta⁸ showed that the chloroform extract of dried cabbage, heated in aqueous suspension in nitrogen gas, reduces indophenol. Ascorbic acid oxidase destroys this reducing action. Guha and Sen-Gupta⁹ estimate from the results of biological tests that 60 to 70 per cent of the indol-reducing value of the dried chloroform extract is due to *ascorbigen*.

Vitamin D.—See also Volumes II, p. 21; III, p. xxii. The formula for *cholesterol*, Volume III, p. 282, also of various sterols, is of interest in this connection.

¹ Protoplasma 1937, **28**, 516.

² Ind. Eng. Chem. 1937, **29**, 189, 1195.

³ Science 1938, **87**, 214.

⁴ Ibid. 1937, **86**, 540.

⁵ Deut. Med. Wochenschr. 1932, No. 22.

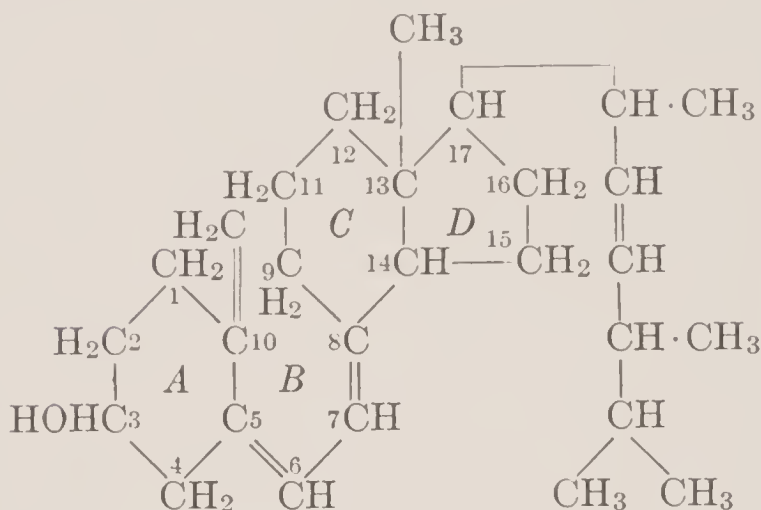
⁶ Nature 1936, **137**, 946.

⁷ Ibid. 1936, **138**, 933.

⁸ Science and Culture 1937, **3**, 59, 63.

⁹ Nature 1938, **141**, 974.

Heilbron, Jones, Samant, and Spring¹ give the following formula for *calciferol* differing from that of Windaus and Thiele (Volume III, p. xxii) in the structure of the sugar chain:



Calciferol (Heilbron et al.)

A natural vitamin, D_3 , forms 80 per cent of the antirachitic power of butter fat, hay, and cow liver, according to Rygh.² It is not absorbed by animal charcoal as is irradiated ergosterol. Windaus, Lettré, and Schenck³ and Windaus, Schenck, and V. Werder,⁴ by irradiation of cholesterol also obtained vitamin D_3 which appeared to conform in antirachitic power to the natural vitamin. The transition product (provitamin) of the process was shown to be *7-dehydrocholesterol*, differing from cholesterol (Volume III, p. 282) in that a double bond is inserted between 7 and 8 with elimination of a hydrogen at each of these numbers. Later Schenck⁵ prepared crystalline vitamin D_3 from the *m*-nitrobenzoate, with activity greater than that of calciferol. Koch and Koch⁶ demonstrated the presence of 7-dehydrocholesterol, or a similar substance with two double bonds in ring B, as an impurity of crude cholesterol. Since it exhibited four absorption bands, it was not ergosterol. Provitamin D was present in heated, purified cholesterol, but it did not show the double bonds.

Brockmann⁷ isolated from fish-liver oils, and Windaus and Bock⁸

¹ J. Chem. Soc. 1936, p. 905.

² Z. Vitaminforsch. 1934, **3**, 164.

³ Ann. 1935, **520**, 98.

⁴ Z. physiol. Chem. 1936, **241**, 100.

⁵ Naturwissensch. 1937, **25**, 159.

⁶ J. Biol. Chem. 1936, **116**, 757.

⁷ Z. physiol. Chem. 1936, **241**, 104; 1937, **245**, 96.

⁸ Ibid. 1937, **245**, 168.

from pig skin, what they regarded as natural vitamin D₃, although Bills, also Bills and Massengale, and Imboden,¹ had previously found that the vitamin D of blue-fin tuna oil is not the same as that of cod- and halibut-liver oils.

Results by Brockmann² indicate that *vigantol* (vitamin D₃) is twice as effective for infants as *calciferol* (vitamin D₂).

According to Müller,³ both the second (*tachysterol*) and third (vitamin D) irradiation products formed from ergosterol have three of the four double bonds in rings A and B, although not in the same place. One double bond results from the opening of the B ring of ergosterol; when on heating vitamin D at 188° C. the ring is closed, two isomeric substances (C₂₈H₄₄O), *isopyrovitamin* and *pyrocalciferol*, are formed. The final products of the irradiation of vitamin D are believed to be *toxisterol* and the two *suprasterols* (I and II) of Laquer and Linsert.⁴

Rothenheim⁵ and Bills discuss eight forms of vitamin D.

From irradiated 22-dehydroergosterol Windaus and Trautmann⁶ obtained crystalline vitamin D₄ with the formula C₂₈H₄₆O, the probable structure analogous to that of D₂, and the following properties: melting point 107 to 108° C., specific rotation at 18° C. —89.3°, and absorption maximum at 2650 Å.

The distillation and biological results of Hickman and Gray⁷ indicate that cod-liver oil contains 6 vitamins of the D group and that other fish-liver oils contain still others. The lowest-boiling-point vitamin D probably lacks the side chain at 17.

Koch, Koch, and Ragins,⁸ Waddell,⁹ Hathaway and Lobb,¹⁰ and Haman and Steenbock¹¹ regard cholesterol, not ergosterol, as the natural precursor of vitamin D, and Windaus, Lettré, and Schenck¹² confirmed this view by the preparation from cholesterol, by a complicated process, of 7-dehydrocholesterol, and from the latter, by irradiation,

¹ Science 1934, **80**, 596; J. Am. Med. Ass. 1937, **108**, 13.

² Klin. Wochenschr. 1937, **16**, 1383.

³ Z. physiol. Chem. 1935, **233**, 223.

⁴ Klin. Wochenschr. 1933, **19**, 753.

⁵ Pharm. Monatsh. 1937, **18**, 105.

⁶ Z. physiol. Chem. 1937, **247**, 185.

⁷ Ind. Eng. Chem. 1938, **30**, 796.

⁸ J. Biol. Chem. 1929, **85**, 141.

⁹ Ibid. 1934, **105**, 711.

¹⁰ Ibid. 1936, **113**, 105.

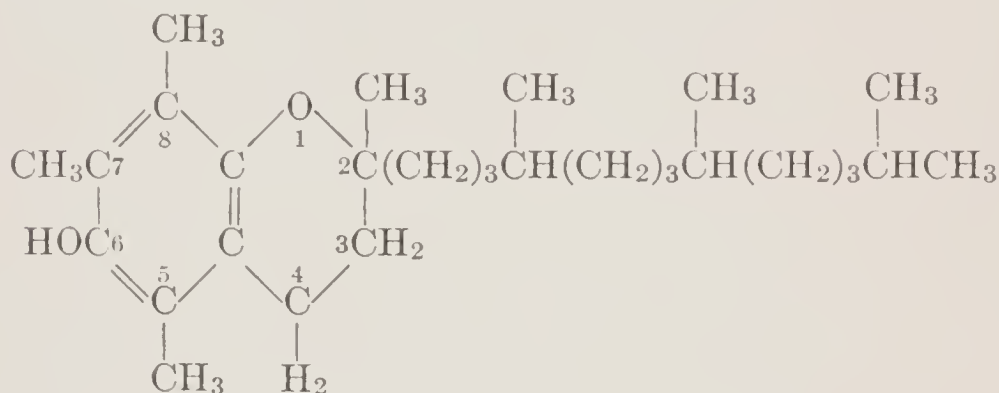
¹¹ Ibid. 1936, **114**, 505.

¹² Ann. 1935, **520**, 98.

of a highly active derivative. Milas and Heggie,¹ by the simple reaction of cholesterol acetate with benzoquinone, obtained 7-dehydrocholesterol as the first step, before securing by irradiation a large yield of the vitamin.

Vitamin E.—See also Volumes II, p. 22, and III, p. xxiii.

Grijns and Dingemanse² believe that there are two substances with vitamin E activity, one essential for male, the other for female fertility, but neither has been isolated; there is, however, good evidence that, like vitamins A and D, several substances have vitamin E activity. Investigations of the past few years led up to the following formula for one of these substances:



α -Tocopherol (Farnholz)

Olcott³ has shown that the absorption spectrum band at 2940 A of concentrates from wheat germ and cottonseed oils is not due to a physiologically active constituent. His results indicate that a single vitamin containing one or more hydroxyl groups and combining with acetic and benzoic acids to form active esters is present.

A vitamin concentrate, separated by Drummond, Singer, and Mac-Walter⁴ from the unsaponifiable matter of wheat germ oil, was a pale yellow viscous oil, which showed a polycyclic structure with one oxygen atom forming an acetyl derivative and another inactive, also three double bonds, reacting with hydrogen and iodine. Results of spectroscopic examination suggest a hydroxyl group in a keto-enolic structure. The absorption maximum at 2940 A, recorded in the first paper, was shown in the second paper to increase with a decrease in biological activity.

¹ J. Am. Chem. Soc. 1938, **60**, 984.

² Proc. Acad. Sci. Amsterdam 1933, **36**, 242.

³ J. Biol. Chem. 1934, **107**, 471; 1935, **110**, 695.

⁴ Biochem. J. 1935, **29**, 456, 2510.

Evans, Emerson, and Emerson¹ suggested the name *α-tocopherol* (indicating fertility) for an alcohol, $C_{29}H_{50}O_2$, obtained as a light-colored viscous oil showing an absorption band at 2980 Å, by hydrolysis of one of the three allophanates separated from the unsaponifiable matter of wheat germ oil. Continuing the work, Emerson, Emerson, Mohammed, and Evans² isolated the allophanates with properties and sources as follows: *α-tocopherol allophanate*, melting point 158 to 160° C. (wheat germ oil, cottonseed oil, palm oil, lettuce leaves); *β-tocopherol allophanate*, melting point 144 to 146° C. (uncor.), specific rotation at 25° C. 5.7° (wheat germ); and *γ-tocopherol allophanate*, melting point 138 to 140° C., specific rotation at 20° C. 3.4° (cottonseed oil).

John³ isolated *cumo-tocopherol*, $C_{28}H_{48}O_2$, a new fraction of vitamin E, and showed that it is a monoether of pseudocumohydroquinone and the next lower homolog of *α-tocopherol*.

The structural formula for *α-tocopherol* ($C_{29}H_{50}O_2$) given herewith is that proposed by Fernholz⁴ and approved by Smith, Ungnade, and Prichard,⁵ Evans, Emerson, and Emerson,⁶ and Emerson.⁷ The formula of Karrer, Fritzsche, Ringier, and Salomon⁸ differs from this chiefly in that the oxygenated part of the double ring, lacking the angle with CH_2 at 4, is five instead of six sided, that is, the vitamin is considered to be a coumarane, not a chromane.

Kimm⁹ obtained white crystals from rice germ oil concentrates. A difficultly soluble fraction ($C_{40}H_{51}O_2$) of the crystals, melting at 156° C., yielded, on hydrolysis with alcoholic potash, a substance with vitamin E activity. Ueno, Ota, Yokoyama, and Matsuda¹⁰ isolated from rice oil a substance, similar to the vitamin E fraction of Evans and Burr, to which they ascribe the preliminary formula $C_{30}H_{52}O$.

Vitamin G (B_2) or *Riboflavin*, $C_{17}H_{20}N_4O_6$.—See also Volumes II, p. 22, and III, p. xxiii.

¹ J. Biol. Chem. 1936, **113**, 319.

² Ibid. 1937, **122**, 99.

³ Z. physiol. Chem. 1937, **250**, 11.

⁴ J. Am. Chem. Soc. 1938, **60**, 700.

⁵ Science 1938, **88**, 37.

⁶ Ibid. p. 38.

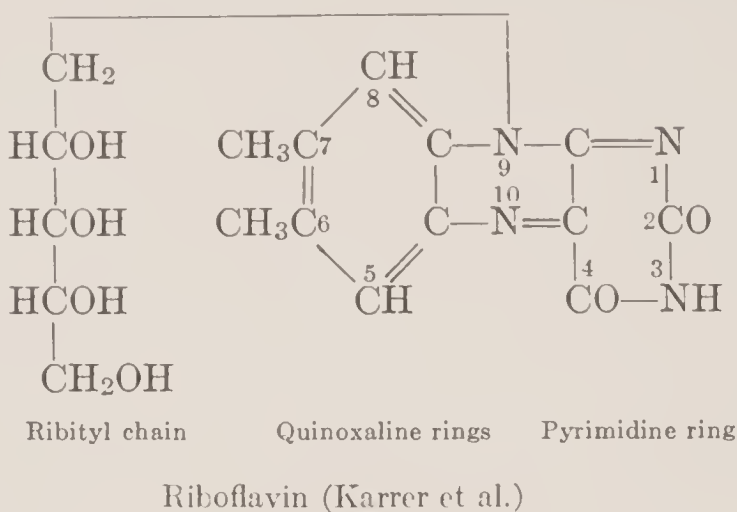
⁷ Ibid. p. 40.

⁸ Helv. Chim. Acta 1938, **21**, 520.

⁹ Sci. Papers Inst. Phys. Chem. Res. (Tokyo) 1935, **28**, 74.

¹⁰ J. Soc. Chem. Ind. Japan 1935, **38**, Suppl. bind. 190.

The more fully descriptive name of this important vitamin, a dione (diketone) with a sugarlike side chain, is 6,7-dimethyl-9[*d*-1'-ribityl]-isoalloxazine in conformity to the configuration shown below:



Of the three rings, two are rectangular in conformity to long usage and not hexagonal as given in Chemical Abstracts and by Karrer; the numbering, however, is strictly that followed by Karrer and not by Chemical Abstracts. See Johnson.¹

A brief summary of the most important results obtained in the laboratories of Kuhn, Karrer, and v.Euler, which, together with data given in Volume II, warrant the above formula, follows:

Kuhn and Rudy² confirmed the synthesis of 6,7-dimethyl-xylityl-alloxazine made by Stern, Holiday, and Stern³ and also produced the substance by the action of light on lactoflavin. Kuhn and Weygand⁴ synthesized methyl isoalloxazines, with arabityl and xylityl chains, similar to lactoflavin. Karrer, Schöpp, Benz, and Pfaehler,⁵ in the following year, reported the synthesis of methyl and dimethyl isoalloxazines with arabityl, xylityl, and sorbityl side chains, culminating with 6,7-dimethyl-9-[*d*,1'-ribityl]-isoalloxazine which was thought possibly to be identical with natural lactoflavin. V.Euler, Malmberg, Becker, and Frei⁶ were then added to the group of workers and by biological methods they proved that the two actually are identical, agreeing in chemical, physical, and growth-promoting properties, but they reserved opinion as to the antipellagric efficiency. They reported

¹ Pyrimidines, etc., in Gilman's Organic Chemistry, New York, 1938, p. 1013.

² Ber. 1934, **67B**, 1826, 1936.

³ Ibid. pp. 1442, 1449.

⁴ Ibid. pp. 1409, 1939.

⁵ Ibid. 1935, **68B**, 216; Helv. Chim. Acta 1935, **18**, 69, 426.

⁶ Helv. Chim.-Acta 1935, **18**, 522.

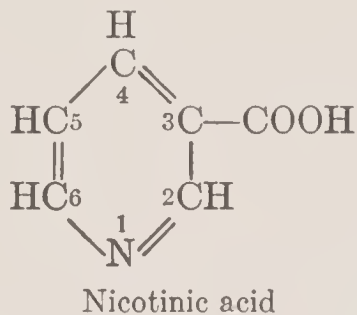
that 6,7-dimethyl-arabityl-isoalloxazine promoted growth slightly, but that the other synthetic flavins mentioned above, also 6,7-dimethyl-rhamnityl- and 7-methyl-mannityl-isoalloxazines, had no growth action. The identity of synthetic and natural flavins was verified by Kuhn, Reinemund, Kaltschmidt, Ströbele, and Trischmann¹ and Karrer, Salomon, Schöpp, and Benz,² thus ending an intensive competition with divided honors.

As synthesized by György,³ ribo-flavin was as potent as natural lactoflavin, but arabino-flavin was much less potent.

The specificity of lactoflavin is treated by Kuhn, Desnuelle, and Weygand⁴ in two papers, one dealing with the position of the methyl group, the other with the substitution of the methyl group by tetramethylene and trimethylene rings.

Results of experiments by György⁵ appear to discredit the theory that lactoflavin is the preventive of pellagra. He terms the antipellagra factor B₆. Harris⁶ confirms György's findings.

Nicotinic Acid, C₅H₄N · COOH.—This vitamin, unlike the others, is not a new substance discovered by intensive research with the purpose of placing vitamins on a sound chemical basis. It is a white crystalline powder melting at 228 to 229° C., readily soluble in hot water and hot alcohol, but only slightly soluble in ether. Its structural formula follows:



Dann,⁷ in a preliminary note on his work in collaboration with Subbarow, states that the preventive of rat dermatitis and the preventive of chick dermatitis have been distinguished but not identified. He confirms the evidence of Elvehjem, Madden, Strong, and Woolley⁸

¹ Naturwissenschaften 1935, 23, 260.

² Ibid. p. 355.

³ Z. Vitaminforsch. 1935, 4, 223.

⁴ Ber. 1937, 70B, 1293, 1302.

⁵ Biochem. J. 1935, 29, 741.

⁶ Ibid. p. 776.

⁷ Science 1937, 86, 616.

⁸ J. Am. Chem. Soc. 1937, 59, 1767.

that nicotinic acid prevents blacktongue, but not the conclusion of Koehn and Elvehjem¹ that it also cures chick dermatitis. He believes that nicotinic acid is the pellagra preventive; if it is not, another member must be added to the B group.

Vitamin H.—As described by Booher,² this is a heat-stable constituent of the vitamin B complex. It combines the properties of Elvehjem's precipitate factor from liver, the so-called filtrate factor, and B₆, preventing erythredemic dermatosis and promoting growth.

Vitamin K.—Dam and Schönheyder³ name green vegetables as good sources of fat-soluble vitamin K. Cold saponification greatly decreases, hot saponification entirely destroys, its activity. Dam⁴ states that the factor prevents the bleeding disease of barnyard fowls. Its deficiency is not related to *hemophilia congenita*.

Almquist and Stokstad⁵ give detailed instructions for the determination of vitamin K in feeds.

Vitamin L.—Of the two lactation vitamins identified by Nakahara, Inukai, Ugami,⁶ L₁ was separated from beef liver and L₂ from baker's yeast. In both cases the vitamin B complex was first removed by adsorption on acid earth and both forms of vitamin L finally precipitated with phosphotungstic acid with an intermediate precipitation by barium hydroxide.

Vitamin P or Citrin.—Szent-Györgyi, collaborating with Rusznyák and Benthásáth,⁷ discovered in lemon juice and paprika a flavone color or flavonol glucoside, related to hesperidin, dimethylohesperidin, and quercitrin, which prevents pathological permeability of blood capillaries. It appears to act only in conjunction with vitamin C, since the symptoms of scurvy due to lack of both C and P are different from those due to absence of C alone from an otherwise complete dietary. This may explain the failure of Zilva⁸ to delay the appearance or prevent the fatal termination of scurvy by adding citrin to a scorbutic diet.

Lajos and Gerendas⁹ state that the spectrum of citrin is a composite of the spectra of hesperidin and eriodictyol, both flavone gluco-

¹ J. Biol. Chem. 1936, **118**, 693.

² Ibid. 1937, **119**, 223.

³ Biochem. J. 1936, **30**, 897.

⁴ Angew. Chem. 1937, **50**, 807.

⁵ J. Nutrition 1937, **14**, 235.

⁶ Science 1938, **87**, 372.

⁷ Nature 1936, **138**, 27, 798; 1937, **139**, 326; 1937, **140**, 426.

⁸ Biochem. J. 1937, **31**, 915.

⁹ Biochem. Z. 1937, **291**, 229.

sides with a first absorption band between 2780 and 2900 A, common to the group, and a second band of variable position.

Moll¹ questions the existence of this vitamin.

Vol. II, p. 698; Vol. III, p. xxv. **Vitamins in Oranges.**—*Carotene.*—Taylor and Witte² sampled oranges from California and Florida, from November 1935 to June 1936 and from November 1936 to January 1937 inclusive, as they arrived on the New York market. Without delay they carried out determinations of carotene in the screened juice by Guilbert's method, after demonstrating that there is no loss of carotene during concentration in a current of air. A summary of their results follows:

California oranges, Valencia, 14 samples, size 176 to 220, carotene 0.65 to 2.74, aver. **1.65** mg. per liter; Washington Navel, 68 samples, size 126 to 252, carotene 0.24 to 2.97, aver. **1.07** mg. per liter.

Florida oranges, Valencia, 34 samples, size 200 to 252, carotene 0.18 to 1.05, aver. **0.57** mg. per liter; Pineapple, 32 samples, size 90 to 288, carotene 0.10 to 0.83, aver. **0.34** mg. per liter; Early Rounds, 8 samples, size 176 to 252, carotene 0.20 to 0.39, aver. **0.32** mg. per liter; Hamlin Seedless, 2 samples, size 176, carotene 0.16 to 0.17, aver. **0.17**; Parson Brown, 2 samples, size 176, carotene 0.15 to 0.42, aver. **0.29** mg. per liter; Florida Temple, 2 samples, size 76 to 150, carotene 0.23 to 0.70, aver. **0.47** mg. per liter; Jaffa, 1 sample, size 250, carotene 0.27 mg. per liter; and Homasassa, 1 sample, size 250, carotene 0.53 mg. per liter.

Ascorbic Acid.—An "Abstract from a Part of Citrus Fruit Studies" by Arthur W. Thomas and M. Irene Bailey, kindly furnished by the senior author, was further condensed as follows: From November 1936 to May 1937, 19 boxes of Florida and 18 boxes of California oranges were analyzed. All were as found on the market in New York except 4 boxes of the Florida oranges which were shipped direct from Florida and all were U. S. No. 1 grade fruit. The fruit was gauged for size, and all imperfect specimens eliminated. Division of the contents of a box into at least three groups according to size was made, and 36 oranges for analysis were selected *pro rata* to size from these groups. After each orange was weighed, the juice was promptly expressed in a "No. 31 Arnold Model Extractor." The weight and volume of the juice and vitamin C content were determined. Both the "2,6-dichlorophenolindophenol" dye and the iodine titration methods were employed, but only the results by the former method were submitted.

¹ Klin. Wochenschr. 1938, **16**, 1653.

² Ind. Eng. Chem. 1938, **30**, 110.

Florida oranges, size 150, All Specimens, Pineapple (including 1 box Cunningham Sweet), and Valencia gave respectively: No. of boxes 19, 10, and 9; weight per orange 272, 269, and 275 grams; weight of juice 154, 148, and 160 grams per orange; per cent of juice by weight of orange 56.6, 55.0, and 58.2; volume of juice per orange 148, 142, and 154 cc.; vitamin C 0.528, 0.563, and 0.489 mg. per cc. or 78.1, 79.9, and 75.3 mg. per orange.

California oranges, size 126, All Specimens, Navel, and Valencia gave respectively: No. of boxes 18, 16, and 2; weight per orange 272, 274, and 259 grams; weight of juice, 123, 121, and 138 grams per orange; per cent of juice by weight of orange 45.2, 44.2, and 53.3; volume of juice per orange 118, 116, and 133 cc.; vitamin C 0.547, 0.550, and 0.516 mg. per cc. or 64.6, 63.8, and 68.6 mg. per orange.

The authors conclude, within the scope of their investigation: "(1) The All Specimens averages were Florida 1.25 times as much volume of juice as California; . . . (2) In Vitamin C content, the juice of the California oranges per unit volume of juice was 1.036 times as potent as that of the Florida oranges, but, *per orange*, the Floridas were 1.21 times richer in Vitamin C than the Californias. (3) . . . Florida Pineapple orange juice *per unit volume* was found to be 1.024 times as rich in Vitamin C as the California Navel juice and the Pineapple oranges yielded 1.25 times as much Vitamin C *per orange* as the Navels."

Vol. III, p. 236. **Egg White Proteins.** I *Ovalbumin*.—Wu and Yen¹ observed that the albumin of poultry eggs is changed in solubility by *N*/20 hydrochloric acid and sodium hydroxide. Wu and Wu² showed that denaturation by heat, acid, and alkali is accompanied by hydrolysis. Wu³ demonstrated that denaturation by heat and by alcohol takes place in two stages: (1) hydrolysis and (2) agglutination, but Wu and Ling⁴ and Wu and Wang⁵ found that this was not true of mechanical (shaking) denaturation, as claimed by Bull and Neurath.⁶ Wu and Wang⁵ and Bull,⁷ differing from Bull and Neurath,⁶ claim that the rate of denaturation does not decrease with the concentration. Bull⁷ employs in his studies an ingenious

¹ J. Biochem. (Japan) 1924, 4, 345.

² J. Biol. Chem. 1925, 64, 369.

³ Chinese J. Physiol. 1927, 1, 81.

⁴ Ibid. p. 407.

⁵ J. Biol. Chem. 1938, 123, 439.

⁶ Ibid. 1937, 118, 163.

⁷ Ibid. 1938, 123, 17.

apparatus consisting of a drum which, by rotating into the solution of the albumin, creates continuously a new surface-denatured layer that by proper regulation of concentration and speed may be made uni-molecular.

II *Conalbumin*.—Wu and Ling¹ separate conalbumin, which forms 10 per cent of the total albumin of egg white, from ovalbumin by shaking which coagulates only the latter.

¹ Chinese J. Physiol. 1927, 1, 431.

PART I
SACCHARINE PRODUCTS

PART I

SACCHARINE PRODUCTS

INTRODUCTION

As is true of other terms applied to the groups into which foods are more or less arbitrarily divided, the term saccharine products calls for definition. As here used it includes all food products consisting essentially of soluble sweet carbohydrates derived directly or indirectly from saccharine, starchy, or inulin-containing stems, tubers, roots, seeds, and flowers—from the last named in the form of honey. It does not include jams, jellies, preserves, and similar saccharine fruit products with or without added sweetening or lactose products.

The carbohydrate in the final product may consist essentially of (1) *sucrose* that existed ready formed in the plant, together with more or less invert sugar derived from sucrose or else representing a stage in the formation of sucrose (e.g., sugar, cane and beet molasses, maple products); (2) *invert sugar* formed by the nearly complete inversion of the sucrose of nectar or commercial sugar (e.g., honey, commercial invert sugar sirup); (3) *dextrose* (*d-glucose*), alone or mixed with *maltose*, and *dextrin*, formed from the polysaccharide starch in a wet way by hydrolysis with dilute acid (e.g., glucose sirup, starch-sugar); (4) *levulose* formed from the polysaccharide inulin by hydrolysis analogously to the formation of dextrose from starch; (5) *maltose* formed by enzymic action on starch (e.g., malt sugar); or (6) *caramel*, an ill-defined group of substances obtained by roasting sugars strongly.

Of the numerous other mono- and disaccharides, some occur in nature more or less widely distributed, but not in such amount as to have commercial significance. Of the trisaccharides, *raffinose* occurs in beet molasses, in cottonseed, sprouted grain, and various other vegetable products. *Dextrin* is considered under Glucose Sirup, and *lactose* under Cow's Milk.

The world's supply of sucrose is obtained chiefly from the sugar cane and the sugar beet, at times in approximately equal amount.

Before the Spanish Conquest of Mexico, the Aztecs made sugar from the stalks of Indian corn (*Zea Mays* L.), and during the Revolutionary War the northern English colonists worked up this same raw material when, owing to embargoes, they were unable to bring in sugar from the West Indies. Along in the seventies of the last century sorghum stalks were advocated by Collier and others as a source of commercial sugar. This member of the grass family still is utilized for the production of sorghum sirup. The stems of various species of palm are sufficiently rich in sugar to warrant commercial production, but as yet are only of local importance.

Horne,¹ in an article entitled "Sugar Industries of the United States," states that 5,134,746 long tons of cane sugar were consumed in continental United States during the year 1934. This is equivalent to 90.71 pounds (41.15 kilos) per capita. His figures on beet sugar are in terms of production during 1933-34, namely, 1,466,053 long tons. He quotes government figures on the production of liquid products during 1931 in terms of thousand gallons as follows:

Cane sirup.....	14,359	Maple sirup.....	2,186
Cane molasses (as food).....	5,168	Maple sugar as sirup.....	202
Sorghum sirup.....	17,818	Corn sirup and mixtures.....	81,686

Dr. Horne, in a personal communication, gives the following figures, from Willett and Gray's Statistical, on the world's production of sugar in long tons:

	1913-14	1927-28	1934-35	1935-36
Cane.....	9,801,536	17,068,739	16,301,100	17,266,333*
Beet.....	8,634,942	9,024,327	9,479,422	9,256,500*

* Estimates.

PHYSICAL PROPERTIES OF SUGARS. Crystallization.—*Dextrose* (*d-glucose*) crystallizes from hot alcohol as the anhydride in needle-shaped crystals melting at about 146° C. From a saturated water solution it crystallizes with one molecule of water, most of which is driven off at 60° C. without melting, the remainder at 100° C. *Levulose* (fructose) crystallizes from alcohol as anhydrous needles, melting at about 100° C. From a concentrated water solution it crystallizes as needles with one-half a molecule of water; these melt at 170° C. with decomposition. *Sucrose* readily separates from the concentrated water solution as large monoclinic crystals, melting at about 170° C.; at a somewhat higher temperature caramelization takes place.

¹ Ind. Eng. Chem. 1935, 27, 989.

Maltose crystals are needle-shaped, contain one molecule of water, and melt at 100° C. on rapid heating. The water is slowly driven off, with decomposition, by gradual heating up to 100° C. or higher. *Raffinose* (melitriose) crystallizes as needles with five molecules of water from a water solution. The crystals melt on rapid heating at about 100° C. but on gradual heating lose the water of crystallization without melting.

Solubility.—One hundred parts of water at 15° C. dissolve about 80 parts of *dextrose*; 100 parts of cold alcohol dissolve less than 2 parts. *Levulose* is more soluble than dextrose, the crystals that form in honey, causing granulation, being dextrose. In hot alcohol levulose dissolves easily, in cold alcohol with difficulty. One hundred parts of water at 15° C. dissolve about 200 parts of *sucrose*; this sugar is slightly soluble in hot alcohol. *Maltose* is readily soluble in cold water. Only about 6 parts of *raffinose* dissolve in 100 parts of water at 15° C.; in hot water, however, raffinose is very soluble.

Sweetness.—The relative values, as determined by Paul,¹ Sale and Skinner,² and Spengler and Traegel,³ follow:

	Sucrose	Dextrose	Levulose	Invert sugar	Maltose	Lactose
Paul.	100	52	103	28
S. and S.	100	52	150	85	60
S. and T.	100	108

It will be noted that Sale and Skinner's value for levulose does not agree with those given by Paul and by Spengler and Traegel, but their values for invert sugar and the average of the values for dextrose and levulose are not far apart.

Polarization.—The specific rotation of the common sugars at 20° sodium light, concisely expressed as $[\alpha]_D^{20}$, follows: *dextrose*, anhydride +52.5, hydrate +48.2; *levulose* −92.5; *sucrose* +66.5; *maltose* about +138; *raffinose* about +104.5. These figures are for constant polarization; immediately after solution the figures are much higher. This phenomenon, known as mutarotation, birotation, or multirotation, is explained in a subsequent paragraph. The time required for constant polarization varies from a fraction of an hour to half a day.

¹ Chem. Ztg. 1921, **45**, 705.

² South. Carbonator and Bottler June 1918; J. Ind. Chem. 1922, **14**, 522.

³ Z. Ver. deut. Zuckerind. 1927, **77**, 1.

The rotation of levulose decreases markedly on increase in temperature, whereas dextrose is little influenced by temperature. At 87° C. the minus polarization of the one counterbalances the plus polarization of the other, hence invert sugar polarizes zero at that temperature. This principle is utilized in detecting glucose in molasses and other saccharine products.

Multirotation.—An important step in the study of sugars was made by the discovery of Tanret¹ that each sugar has an α - and a β -form. Referring to the closed-chain formulas for *d*-glucose as given below, which represent the α -form, the group HCOH at 1 occurs also in the β -form of *l*-glucose at 1, but in the β -forms of both *d*- and *l*-glucose it is replaced by its mirror image HOCH. The existence of α - and β -isomers explains the phenomenon of multirotation, that is, the gradual change in the rotation of the solution of certain sugars until equilibrium is reached. According to Tanret, the specific rotation with D light of the α -form of *d*-glucose (ordinary dextrose) is +110° and of the β -form +19°. When the sugar is first dissolved practically the full polarizing activity of the α -form is obtained, but on standing there is a change, more or less rapid according as the temperature is high or low, to the β -form, until equilibrium is reached, which in a 10 per cent solution occurs when 37 per cent exists as the α - and 63 per cent as the β -form.

To obviate inconsistencies in the use of the designations *d* and *l*, Hudson² has suggested a nomenclature based on the rotatory power of each sugar, in accordance with his observation that the figure obtained by subtraction of the rotation of the β -form from that of the α -form of all sugars related to *d*-glucose is plus, whereas the corresponding figure for all sugars related to *l*-glucose is minus.

CHEMICAL CONSTITUTION OF SUGARS.—The earlier chemists knew little of sugar molecules beyond what was shown by the empirical formulas, but during the past fifty years Tollens and Fischer in Germany, Tanret and Pictet in France, Frankland and Haworth in England, Zemplén in Hungary, and Hudson in the United States, by their discoveries, have made possible structural formulas consistent with theory and practice.

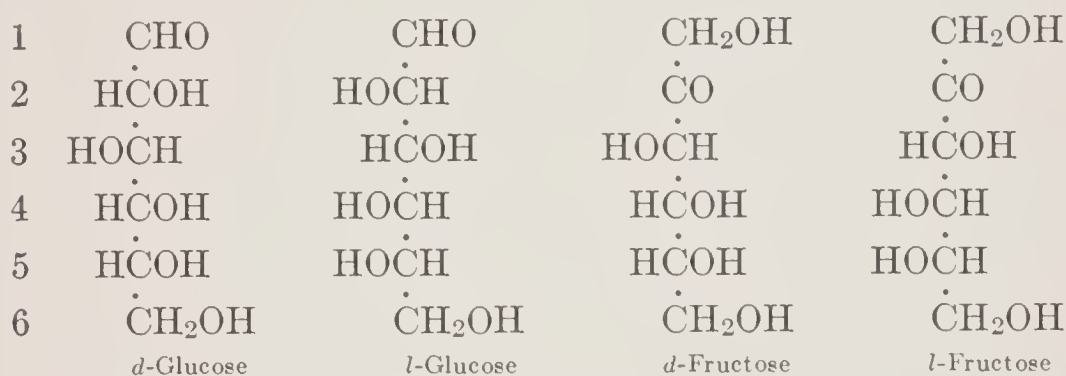
Maltose, lactose, and sucrose have been synthesized by Pictet and

¹ Bul. soc. chim. 1895, [3], **13**, 625, 728; 1896, [3], **15**, 195, 349; 1897, [3], **17**, 802; 1905, [3], **33**, 337.

² J. Am. Chem. Soc. 1909, **31**, 66.

Vogel,¹ by the direct combination of the constituent monosaccharides or their tetroacetates, employing zinc chloride as a catalyst.

Hexoses.—According to Fischer's earlier theories the hexoses are classed as *aldoses* (aldehydes) and *ketoses* (ketones) and for each sugar with the prefix *d* there is a stereoisomer with the prefix *l*, the formula for one, as regards the middle asymmetric members of the chain, being the mirror image of the other. The formulas for *d*-glucose (dextrose) and *d*-fructose (levulose), also for the *l*-form of both sugars, as given below, illustrate Fischer's theories:



Fischer's open-chain formulas

The prefix *d* or *l* does not necessarily indicate the actual polarization of a sugar, but rather whether the initial substance from which it was derived was dextro- or levorotatory. In other parts of this work the terms dextrose and levulose are given the preference over *d*-glucose and *d*-fructose, thus, as shown by Bryant,² conforming to the more common usage and avoiding confusion of *d*-glucose with commercial glucose.

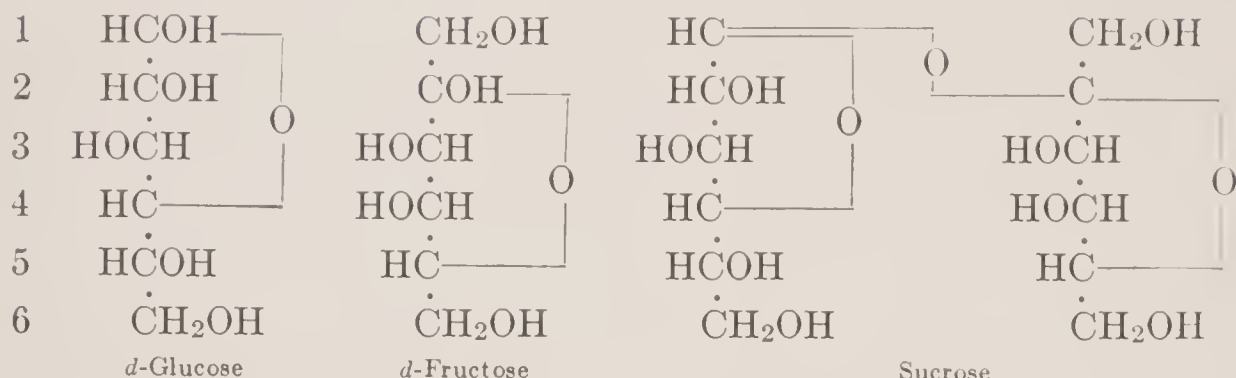
It is a remarkable achievement that of the sixteen members of the aldose series theoretically possible all have been synthesized, although only three exist in nature. Notwithstanding their practical value, the open-chain formulas were later abandoned, even by Fischer himself, in favor of the closed-chain (or equivalent ring) formulas which better represent the actual configuration.

Sucrose and Its Hexose Components.—Tollens suggested formulas for *d*-glucose, *d*-fructose, and sucrose with 4 carbon atoms and 1 oxy-

¹ Compt. rend. 1927, **184**, 1512; 1927, **185**, 332; 1928, **186**, 724; Helv. Chim. Acta 1927, **10**, 588; 1928, **11**, 209, 436.

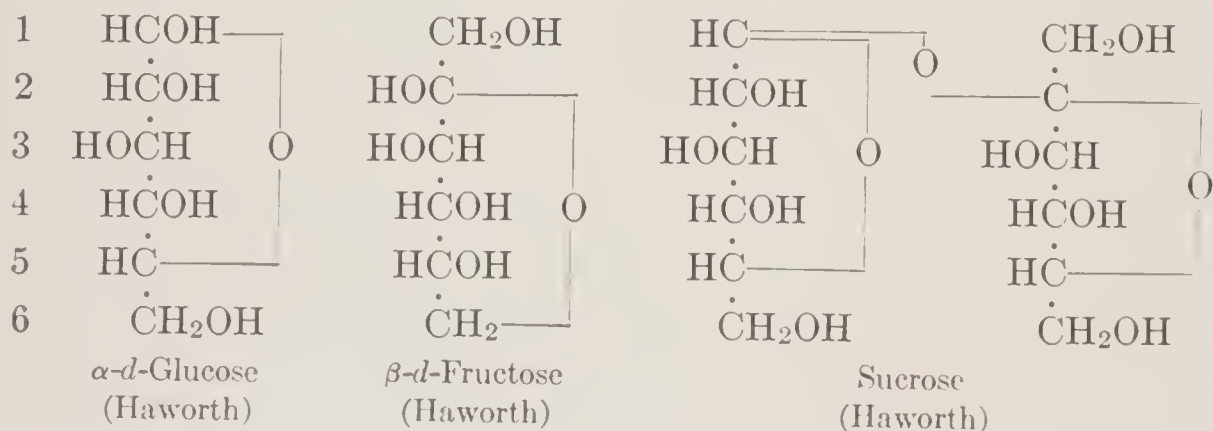
² Ind. Eng. Chem. 1934, **26**, 231.

gen atom in a closed chain (or pentagon), which Fischer further developed to conform to his stereoisomeric theory.



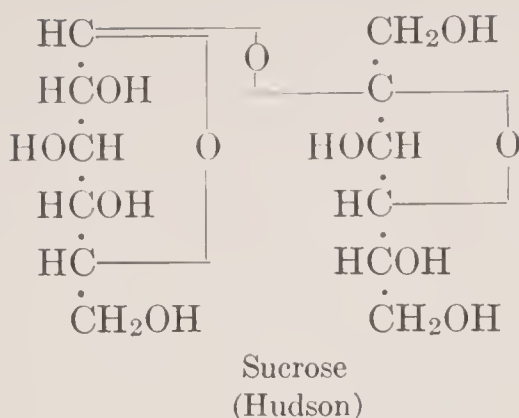
Fischer's closed-chain formulas

More recently Haworth¹ has suggested closed-chain formulas for the monosaccharides with 5 carbons and 1 oxygen in the ring and a new formula for sucrose that conform better with experimental evidence and a study of bead models. Zemplén and some others have accepted Haworth's theories; Hudson,² however, by an application of the rules of isorotation and consideration of other data, derived a formula for sucrose (α -*d*-glucose β -*d*-fructoside) that differs from Haworth's in that the HC of the right-hand (fructose) component with its bridge terminal and the adjoining HCOH are transposed, thus forming a 3-carbon ring.

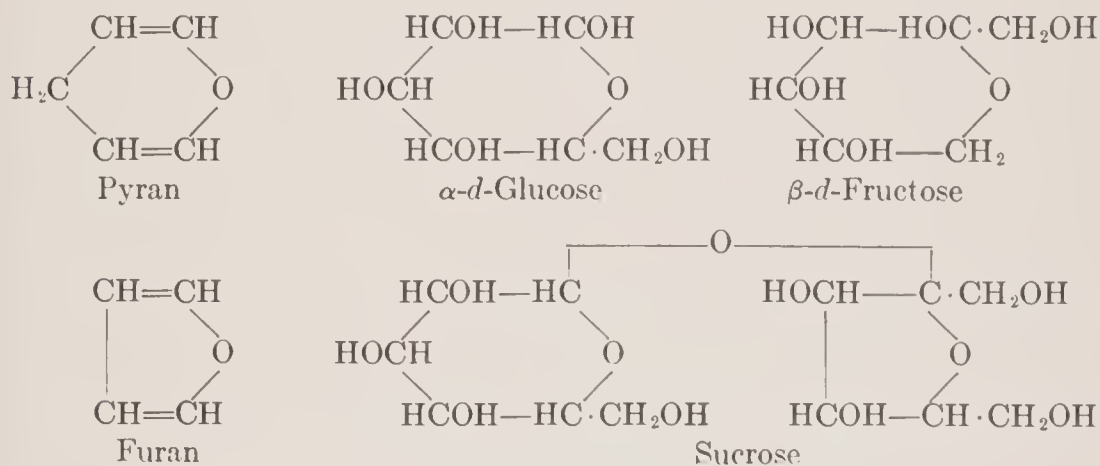


¹ Haworth and Law: J. Chem. Soc. 1916, **109**, 1314; Haworth: *ibid.* 1920, **117**, 199; Haworth and Linnell: *ibid.* 1923, **123**, 294; Haworth and Mitchell: *ibid.* 1923, **123**, 301; Haworth: Nature 1925, **116**, 430; Baker and Haworth: J. Chem. Soc. 1925, **127**, 365; Charlton, Haworth, and Peat: *ibid.* 1926, p. 89; Haworth: The Constitution of the Sugars, London, 1929

² J. Am. Chem. Soc. 1930, **52**, 1707.



According to Haworth's theory, the monosaccharides are related to pyran—glucose is gluco-pyranose, fructose is fructo-pyranose, and galactose is galacto-pyranose—and may be represented as 5-carbon rings, whereas such of the di- and trisaccharides as have a 4-carbon chain show relationship to furan. The structural formulas which follow are so arranged as to facilitate comparison with one another and the other closed-chain formulas given above.

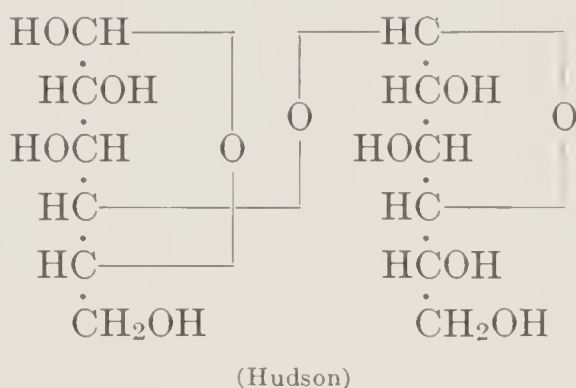
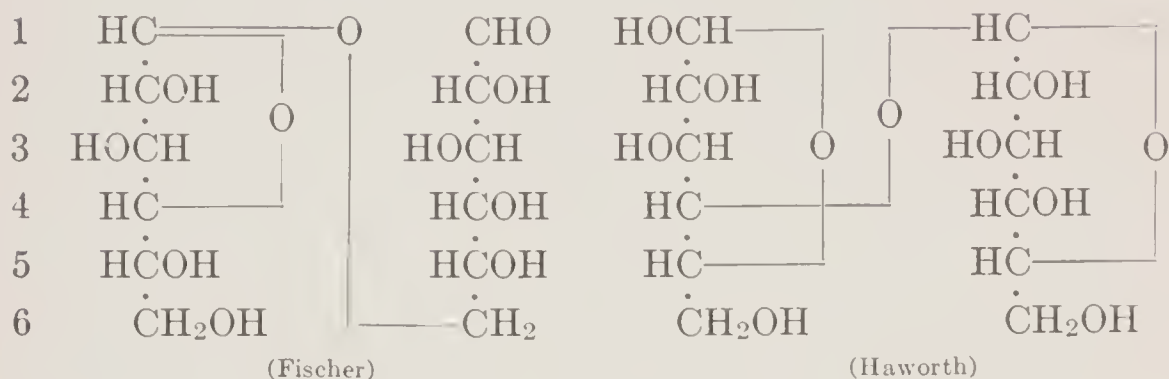


Maltose, $C_{12}H_{22}O_{11} + H_2O$.—Common maltose is a disaccharide analogous to sucrose and lactose, but its components are one molecule each of β - and α -dextrose, or more specifically stated, it is β -*d*-glucose α -*d*-glucoside. It differs from cellobiose in being an α -, not a β -glucoside. The structural formula of Fischer, a second based on the recent theories of Haworth,¹ and a third derived by Hudson² in

¹ Cooper, Haworth, and Peat: J. Chem. Soc. 1926, p. 876; Haworth and Peat: *ibid.* 1926, p. 3094; Haworth: J. Soc. Chem. Ind., 1927, 46, 295T; Zemplén: Ber. 1927, 60B, 1555.

² J. Am. Chem. Soc. 1930, 52, 1707.

conformity to the laws of isorotation, the β part of each being at the left and the α part at the right, follow:



Maltose

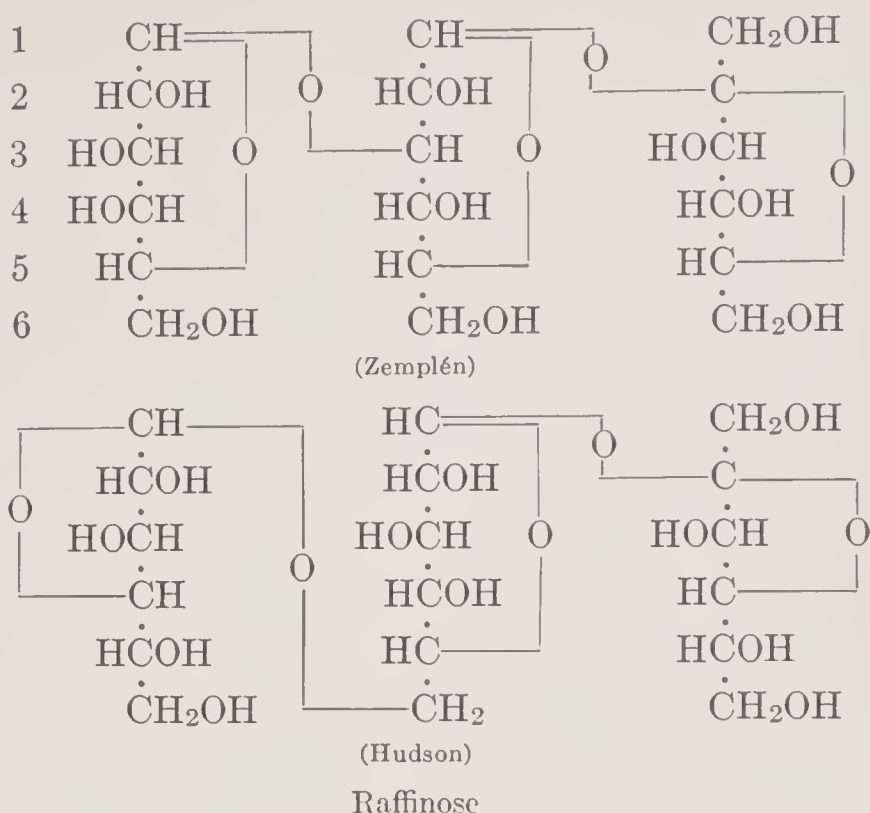
Lactose.—See Cow's Milk, Volume III.

Raffinose, Melitriose, or Gossypose, $C_{18}H_{32}O_{16} + 5H_2O$.—Haworth, Hirst, and Ruell¹ proposed a formula for this trisaccharide, based on the results of cleavage experiments with its methyl derivatives, which Zemplén four years later² revised after studying products of yeast and emulsin hydrolysis. Both formulas agree as to the structure of the galactose group, but not the fructose and glucose groups. It is noteworthy that of the two the Zemplén formula is the more consistent with Haworth's formula for sucrose. A formula derived in the light of isorotation data is that of Hudson.³ In the formulas as given below, the component groups appear in the following order: α -*d*-galactose, α -*d*-glucose, and β -*d*-fructose, the glucose and galactose parts of Zemplén's formula having been reversed to correspond with other formulas herewith.

¹ J. Chem. Soc. 1923, 123, 3125.

² Ber. 1927, 60B, 923.

³ J. Am. Chem. Soc. 1930, 52, 1707.



Chemical Reactions.—Solutions of the monosaccharides (*dextrose*, *levulose*, etc), also of the disaccharides *maltose* and *lactose*, on heating reduce ammoniacal silver solution and alkaline copper solution, give colors with alkalis varying from yellow to dark brown, depending on the time and temperature, and yield, with a solution of phenylhydrazine in dilute sulphurous acid, needle-shaped crystals of an osazone. The relative copper-reducing power is illustrated by the following amounts corresponding to 200 mg. of cuprous oxide (Cu_2O) taken from Munson and Walker's Calculation Table: *dextrose* 89.0, invert sugar 92.0, *lactose* ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) 129.4, and *maltose* ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) 156.5 mg.

Sucrose, a disaccharide, responds to none of these tests, but it is hydrolyzed into invert sugar, that is, equal molecules of *dextrose* and *levulose*, by heating at suitable temperatures with acid or invertase. *Maltose* is also hydrolyzed by similar treatment, two molecules of *dextrose* being formed. *Raffinose*, a non-reducing trisaccharide, on acid hydrolysis yields one molecule each of *levulose*, *dextrose*, and *d-galactose*.

Raybin¹ has recently observed that diazouracil gives with *sucrose*, dissolved in *N*/20 sodium hydroxide, a blue-green color which on addition of a drop of magnesium sulphate is adsorbed by the precipitated magnesium hydroxide; numerous related substances gave no reaction.

¹ Ibid. 1933, 55, 2603.

SUGAR CANE PRODUCTS

THE sugar cane (*Saccharum officinarum* L.), a member of the grass family, believed to be a native of eastern Asia, is cultivated throughout the warmer regions of the earth. In the subtropics only purple and other dark-cane varieties flourish and these do not usually flower, but in the tropics yellow, green, and other light-cane, as well as dark-cane, varieties grow luxuriantly, although they do not flower freely and ripen seeds only under exceptional conditions. New varieties are developed by crossing and selection; all varieties are propagated by sections of the stalk so cut as to take advantage of the buds at the nodes. After cutting, new shoots (ratoons) are developed from the bases of the canes, hence one planting suffices for several years.

Although the percentage of sucrose increases during growth, as shown by the results of Halligan and Verret tabulated below, it is usually necessary to begin cutting before full maturity is reached in order to extend the harvesting season and thus employ labor and factory equipment to the best advantage. After cutting, the sucrose content diminishes rapidly, especially if the dry lower leaves are burned off before cutting, a procedure that is often followed to facilitate handling.

Manufacture of Crude Sugar.¹—The process consists of five stages: (1) milling, (2) defecation, (3) evaporation, (4) crystallization, and (5) centrifuging.

Milling.—Crushing and expressing between heavy rollers is now almost exclusively employed for obtaining the juice. After thorough trial the diffusion method, which proved successful in beet-sugar manufacture, was abandoned as not suited to the conditions of the cane-sugar industry. The cane is first crushed and shredded between cutting disks or pairs of rollers, with surfaces designed for tearing apart the tissues, in a machine known as the crusher. It then passes to the mills, each consisting of three rolls so arranged as to exert heavy pressure on the shredded cane. Water is usually sprayed on the ma-

¹ Horne (Ind. Eng. Chem. 1935, 27, 989) describes modern processes concisely.

terial as it leaves each mill to facilitate the extraction of the juice. From half to two-thirds of the juice is removed by the crusher and the first mill.

The *bagasse*, obtained by the crushing and milling operations, is used for fuel under the boilers at the factory, for the manufacture of sheets of insulating building material, and for various purposes where a raw material consisting chiefly of cellulose is required.

Defecation.—Many methods of clarification, employing a great variety of chemicals, have been devised, but in Cuba *liming* (treatment with calcium hydroxide and heating to about 94° C.) has survived all others, and in Louisiana *sulphitation* (addition of sulphur dioxide), coupled with liming and heating to 100° C., also in some cases with addition of sodium phosphate, is commonly practiced. The excess of lime may be precipitated by carbon dioxide, an operation known as *carbonatation*. Clarifiers recently exploited include basic aluminum carbonate, proposed by Levy,¹ gelatinous silicic acid in conjunction with calcium silicate, recommended by Dekker and Nicola,² and sodium aluminate, studied by Wayne.³

Defecation with lime, as stated by Browne,⁴ precipitates sulphur and impurities such as fiber, fat, wax, dirt, chlorophyll, etc., coagulates proteins and nucleins, and removes part of the gums and ash constituents. By the action of lime and heat, a part of the nucleins are decomposed into nitrogenous bases or purines; variable amounts of reducing sugars are destroyed with formation of soluble salts of lactic, saccharinic, glycinic, and other acids; and some of the sucrose is dehydrated with the formation of caramel. An excess of lime causes the so-called burnt-lime flavor.

Part of the impurities separating on defecation rise to the surface, while others form a mud on the bottom. The clear liquid between is readily separated, but the scum and the mud require filtration.

Evaporation.—In primitive factories the juice is concentrated in open kettles to the point where crystals of sucrose are formed, but in modern factories the evaporation is first carried out in steam-heated multiple-effect vacuum pans to a water content of about 45 per cent.

Crystallization.—The final concentration to grain, that is, to the crystallizing point, is carried out in single-effect vacuum pans. The

¹ Bul. ass. chim. suc. dist. 1923, **41**, 224.

² Arch. Suikerind, Mededeel. Proefsta. 1928, p. 721.

³ Facts About Sugar 1931, **26**, 168.

⁴ J. Am. Chem. Soc. 1919, **41**, 1432.

mass of crystals in the sirupy mother liquor or molasses is known as *massecuite*.

Centrifuging.—Separation of the raw sugar or muscovado from the molasses is effected by centrifugal apparatus. The highest-grade raw sugar is obtained by skillful removal of the adhering molasses by washing. The product is shipped in burlaps to the refineries at the principal ports or, as practiced by Hershey in Cuba, to a nearby refinery. Raw sugar ordinarily contains 94 to 98 per cent of sucrose, rarely less and still more rarely more, the average as received at the port of New York being about 95 per cent. According to Steuerwald,¹ the Java Experiment Station defines standard muscovado as consisting of 95.1 per cent of sugar crystals surrounded by molasses of a sucrose purity of 37.1 per cent.

Sugar Refining.—The process of refining crude sugar is really one of preparing a nearly chemically pure product with the minimum loss of sucrose and the recovery of the impurities in the form of by-products. In conducting the operations no little skill is required. As in the defecation of the juice by certain processes, calcium hydroxide, in the form of milk of lime, and phosphoric acid, in the form of the free acid or calcium monophosphates, serve as clarifiers. The lime combines with the organic acids, and the excess is precipitated by the phosphoric acid or its acid salt. After removal of the precipitate by filtration through special cloth filters, the final clarification is effected by passing through bone black which decolorizes the sucrose solution and removes certain other impurities, notably albumin, gums, carbonates, phosphates, and sulphates. Albumin and blood, formerly common refining agents, are no longer used. The final product obtained by crystallization ranks as regards purity with the highest grades of starch and common salt.

Coates² calls attention to the occasional practice of bringing raw sugar from the tropics and refining without bone black in Louisiana sugar houses during the idle season.

CHEMICAL COMPOSITION.—Analyses of the different parts of the plant, by Halligan and Agee, given by Browne and Blouin,³ follow:

¹ Arch. Suikerind. 1920, **28**, 794.

² J. Ind. Eng. Chem. 1921, **13**, 147.

³ Louisiana Agr. Exp. Sta. 1907, Bul. **91**, 3.

COMPOSITION OF PARTS OF THE SUGAR CANE PLANT (HALLIGAN AND AGEE)

	Water	Protein	Fat and wax	Sugars, etc.	Crude cellulose	Lignin	Pentosans	Ash
	%	%	%	%	%	%	%	%
Leaves.....	74.38	1.70	0.69	2.20	9.18	4.13	5.49	2.23
Stalks	74.96	0.58	0.38	13.40	4.86	2.14	3.04	0.64
Roots	68.79	1.59	0.54	6.34	9.58	4.25	7.04	1.87
Seeds.....	11.03	8.47	2.01	25.51	21.50	26.26	5.22

The composition of the ash of leaves, stalks, and roots is given in a subsequent section.

The table of analyses by Halligan and Verret, also given by Browne and Blouin,¹ shows the *influence of the stage of growth* on the composition of the cane. Sucrose and fiber increase, and ash, acids, pure protein, amides, and gums decrease, throughout growth. Dextrose increases for several months but ultimately decreases.

COMPOSITION OF SUGAR CANE AT DIFFERENT STAGES OF DEVELOPMENT
(HALLIGAN AND VERRET)

	Weight stalk	Pure protein	Amides	Sucrose	Dextrose	Levulose	Acids	Gums	Fiber	Ash
	g.	%	%	%	%	%	%	%	%	%
July 19.....	544	0.10	0.08	1.50	1.72	1.69	0.26	0.19	3.84	0.57
Aug. 2.....	584	0.09	0.04	2.14	1.75	1.64	0.25	0.17	4.32	0.49
Aug. 17.....	916	0.08	0.06	4.88	4.75	1.49	0.22	0.13	6.36	0.48
Sept. 1.....	1364	0.06	0.04	6.07	1.72	1.38	0.22	0.16	0.49
Oct. 3.....	1431	0.07	0.03	8.59	1.85	1.31	0.20	0.07	7.96	0.42
Oct. 17.....	1243	0.08	0.04	11.04	1.05	0.87	0.18	0.09	8.18	0.43

The stage of development noted above has the same general influence on the composition of the juice as on the composition of the cane.

The *influence of climatic conditions* is also marked, as shown by results on the juice obtained by Browne and Blouin,² given herewith. The low temperature and deficiency of rainfall in the Fall of 1903 were adverse to growth but hastened ripening and increased the sucrose

¹ Ibid. p. 13.

² Ibid. p. 22.

content, whereas the warm weather and abundant rains in the Fall of 1904 promoted growth but retarded ripening and decreased the sucrose.

COMPOSITION OF SUGAR CANE JUICE DURING TWO YEARS
(BROWNE AND BLOUIN)

	1903			1904		
	Sucrose	Dextrose	Purity *	Sucrose	Dextrose	Purity *
	%	%	%	%	%	%
Aug. 1.....	2.70	3.80	36.00	2.35	4.04	32.28
Sept. 1.....	5.97	3.68	57.02	5.13	3.75	52.35
Oct. 1.....	11.27	2.51	76.72	8.04	3.55	66.61
Nov. 1.....	13.60	1.02	87.85	9.13	2.82	71.55
Nov. 15.....	15.86	0.63	92.10	12.00	1.66	80.53

* Percentage of sucrose in dry matter.

In general, Cuban cane is richer in sucrose than Louisiana cane.

Analyses by Agee and Hall, given by Browne and Blouin,¹ bring out strikingly the decrease in sucrose and the increase in dextrose from butt to top. The juice of the bottom or first joint of 4 varieties contained, respectively, 10.20, 12.35, 14.80, and 14.40 per cent of sucrose and 1.25, 0.96, 0.42, and 0.25 per cent of dextrose, whereas that of the top or sixteenth joint contained 5.40, 5.50, 4.20, and 5.50 per cent of sucrose and 1.53, 2.00, 2.12, and 3.03 per cent of dextrose.

The table given herewith shows the calculated yield and composition of Louisiana cane juice of average composition and the products made therefrom as obtained by Browne and Blouin.²

It will be noted that the juice contains solids 15 and sucrose 12 per cent. In the original publication are also given corresponding data for a low-grade juice, containing solids 13.50 and sucrose 10.00 per cent, obtained at the beginning of the season, and for a high-grade juice, containing solids 15.50 and sucrose 13.50 per cent, obtained toward the end of the season. The calculations were on the basis of 1,000,000 pounds of cane, an extraction of 75 per cent, and an average solids content in sirups, molasses, and massecuites of 50, 80, and 90 per cent respectively. The yields as here given are in round numbers, omitting the last three figures.

¹ Ibid. p. 29.

² Ibid. p. 90.

YIELD AND COMPOSITION OF SUGAR HOUSE PRODUCTS FROM AN AVERAGE JUICE
(BROWNE AND BLOUIN)

	Rela- tive yield	Solids	Pure pro- tein	Amides, etc.	Su- crose	Dex- trose	Levu- lose	Acids, gums, etc.	Ash
	lbs. 1,000	%	%	%	%	%	%	%	%
Cane.....	1,000
Raw juice.....	750	15.00	0.10	0.10	12.00	1.00	0.70	0.65	0.45
Sulphured juice	750	14.80	0.02	0.10	12.00	1.00	0.70	0.58	0.40
Clarified juice..	750	14.70	0.03	0.10	12.00	1.00	0.70	0.42	0.45
Sirup.....	221	50.00	0.09	0.33	40.80	3.20	2.58	1.50	1.50
1st massecuite.	123	90.00	0.13	0.63	73.44	5.70	4.70	2.70	2.70
1st sugar.....	54	98.75	0.01	0.05	96.00	0.80	0.70	0.39	0.80
1st molasses...	71	80.00	0.20	0.94	53.60	8.76	8.00	4.50	4.00
2nd massecuite.	63	90.00	0.21	1.08	60.30	9.43	9.43	5.05	4.50
2nd sugar.....	24	95.50	0.06	0.34	85.00	2.90	3.10	1.60	2.50
2nd molasses...	43	80.00	0.25	1.50	41.70	12.20	12.50	6.50	5.35
3rd massecuite.	38	90.00	0.26	1.70	46.90	13.30	14.50	7.34	6.00
3rd sugar.....	10	94.00	0.07	0.43	80.00	3.80	4.20	2.00	3.50
3rd molasses...	31	80.00	0.38	2.00	31.70	15.00	16.50	8.20	6.30

The figures on the composition of the juice, somewhat more complete than those given in the preceding tables and representing more recent knowledge, together with those of a low-grade molasses, shown herewith, are by Browne ¹:

COMPOSITION OF SUGAR CANE JUICE AND MOLASSES (BROWNE)

	Water	Pro- teoses	N bases*	Am- ides†	Amino acids‡	Other organic acids§	Decom- posi- tion prod- ucts	Su- crose	Invert sugar	Gums and pec- tins	Ash
	%	%	%	%	%	%	%	%	%	%	%
Juice¶....	83.00	0.01	trace	0.05	0.12	0.10	15.00	0.80	0.10	0.45
Molasses..	20.00	0.10	0.40	0.50	1.50	1.50	6.00	30.00	30.00	2.00	8.00

* Guanine, etc. † Asparagine, glutamine, etc. ‡ Aspartic, etc. § Aconitic, etc. || Lactic acid, saccharinic acid, glycinic (glucinic) acid, caramel, etc. ¶ Constituents eliminated in clarification are as follows: proteins 0.05, nucleins 0.03, fiber particles 0.12, fat and wax 0.10, earthy matter 0.06, and chlorophyl, etc., 0.01%.

¹ Loc. cit.

Browne and Blouin¹ determined the nitrogen distribution in cane juice with the following results: albumin N 0.0039, nuclein N 0.0025, albumose N 0.0021, amino acid N (aspartic) 0.0122, amide N (asparagine) 0.0098, ammonia N 0.0024, nitrate N 0.0071, total N 0.0400 per cent.

Sugar. *Raw Sugar.*—Analyses of raw sugar appear in the foregoing tables. Commonly these show 94 to 98 per cent of sucrose, the usual average being 96 per cent.

Browne² has studied the conditions causing the *change in composition* of raw sugar. Of special significance are the percentages of moisture and the nature of the organisms introduced through improper handling. The average composition of 4 samples each of good- and bad-keeping samples on different dates is shown in the table given below:

AVERAGE COMPOSITION OF GOOD- AND BAD-KEEPING SAMPLES OF RAW SUGAR
(BROWNE)

	Polarization	Water (W)	Sucrose * (S)	Invert sugar	Ash	Undetermined	$\frac{W}{100 - S}$
Good-keeping:	°V	%	%	%	%	%	
May 1915...	96.41	0.91	96.68	1.01	0.59	0.82	0.274
Jan. 1916...	96.35	0.88	96.80	0.94	0.58	0.81	0.275
Bad-keeping:							
May 1915...	95.60	1.35	95.93	1.03	0.59	1.10	0.331
Oct. 1915...	94.93	1.35	95.27	1.87	0.56	0.95	0.285
Jan. 1916...	94.79	1.35	95.31	1.92	0.57	0.85	0.288
Aug. 1917...	93.58	1.45	94.30	2.56	0.59	1.10	0.254

* Clerget method.

Zerban³ gives the average sucrose content of the raw sugar examined at the New York Sugar Trade Laboratory as 95.19 per cent in 1910, increasing or decreasing from year to year with a general tendency upward until 1929, when it was 96.57 per cent. His tabulation for five years which follows shows a slightly higher sucrose content in the raw sugar from the Philippines than in that from other regions.

¹ Loc. cit.

² J. Ind. Eng. Chem. 1918, 10, 178.

³ Facts About Sugar 1930, 25, 438.

	1925	1926	1927	1928	1929
	%	%	%	%	%
Cuba.....	96.03	96.04	96.39	96.39	96.60
Puerto Rico.....	96.22	96.39	96.45	96.29	96.32
Philippines.....	96.80	96.79	96.82	96.86	96.75
Miscellaneous.....	95.82	95.86	96.09	96.07	96.35

Raw sugar contains appreciable amounts of water-insoluble substances. Hardin¹ gives 0.017 to 0.423, average **0.159**, per cent as the content of these substances present in numerous samples of 96 degree Cuban centrifugal sugar analyzed at the New York Sugar Trade Laboratory. On the average 87.5 per cent of these impurities was cane fiber and other organic matter and 12.5 per cent mineral matter such as earth, scale, and lime salts.

Brown Sugar.—Within the memory of some still alive, white sugar, whether loaf, granulated, or powdered, was somewhat of a luxury and much of the sugar used in the household was a light brown, soggy product, a common grade being known as C sugar. Wiley and Collaborators² in 1890 to 1892 examined a large number of samples of C sugar containing in general 3 to 6 per cent of water, 85 to 90 per cent of sucrose, and 0.50 to 2.00 per cent of ash. Still lower grades were on the market, and the moist sugar from the bottom of the molasses barrel was not wasted.

White Sugar.—At present the conditions are reversed, white granulated sugar being the standard product and brown sugar a more expensive product commonly sold by the grocer in small cartons for use in special cakes and candies. Even at the time Wiley conducted his investigations, pulverized sugar, polarizing about 100 and containing less than 0.01 per cent of ash and practically no water, was not uncommon. The *U. S. Standards* now require at least 99.5 per cent of sucrose for granulated, loaf, cut, milled, and powdered sugar. Under the last head is doubtless included so-called confectioners' sugar, which is very finely powdered.

The *impurities*, other than water and ash, of the different grades of white sugar occur in such small amount that they are conveniently expressed in parts per million, that is, milligrams per kilogram.

¹ Ind. Eng. Chem. 1924, **16**, 55.

² U. S. Dept. Agr., Div. Chem. 1892, Bul. **13**, Part 6, 651.

Nevertheless, Byall and Ambler,¹ Ambler, Snider, and Byall,² Ambler,³ Ambler and Byall,⁴ and Byall and Ambler,⁵ considering that these minute amounts may have significance when the sugar is used for special purposes such as the manufacture of caramel, carried out a series of analyses, by carefully tested methods, the results of which, obtained on white cane and beet sugar, both refined and direct consumption, although not in all cases the same samples, are summarized below:

MINOR CONSTITUENTS OF WHITE SUGAR

(Results in milligrams per kilo)

	Total N	Pro- tein N	Amino N	Ammono- nia N	Ni- tric N	Ni- trous N	In- org. P ₂ O ₅	Org. P ₂ O ₅	SO ₃	In- org. SO ₂	Org. SO ₂	Labile S*	SiO ₂
Cane:													
Min. . .	4†	0.0†	0.0†	0.0†	0.0†	0.00†	0.0†	0.0†	0.0‡	0.4‡	0.0‡	trace ‡	8.0†
Max. . .	186†	8.4†	10.0†	12.0†	30.0†	0.25†	0.3†	1.1†	0.0‡	0.6‡	0.1‡	1.4‡	53.0†
Beet:													
Min.	0.0§	1.1§	0.0§	trace §
Max.	1188.4§	58.6§	6.0§	2.9§

* As cystine. † Includes beet sugar. ‡ Refined sugar only. § Direct consumption sugar.

In direct consumption cane sugar the above authors found: sulphuric acid (SO₃) 0.19 to 294.9, inorganic sulphurous acid (SO₂) 0.9 to 29.9, organic sulphurous acid (SO₂) 0 to 2.9, and labile sulphur calculated as cystine 0.4 to 3.4 mg. per kilo. Their ash determinations show on refined cane sugar 0.0005 to 0.010, on direct consumption cane sugar 0.012 to 0.061, and on direct consumption beet sugar 0.009 to 0.254 per cent.

Of the impurities of white sugar that cause greater inversion but less caramelization, Ambler and Byall⁶ list sodium, potassium, and calcium chlorides and sulphates, barium chloride, magnesium sulphate, potassium nitrate, dihydrogen potassium phosphate, potassium acid tartrate, and calcium carbonate. Those that are alkaline or become so, such as sodium and potassium carbonates, bicarbonates, nitrites, and sulphites, disodium hydrogen phosphate, and alkaline organic

¹ Ind. Eng. Chem., Anal. Ed. 1931 **3**, 136.

² Ibid. 1931, **3**, 339.

³ Ibid. 1931, **3**, 341.

⁴ Ibid. 1932, **4**, 34.

⁵ Ibid. 1932, **4**, 325.

⁶ Ibid. 1935, **7**, 168.

salts, produce the opposite effects. Ammonium salts, amino acids and their amides, and ferrous salts increase both inversion and caramelization.

By treating sugar crystals of uniform size (secured from samples of various origin) with sugar solutions of different densities below saturation, an analysis of the residue showed that in general over 50 per cent of the ash, sulphates, chlorides, sodium, potassium, and total nitrogen is located in the outer layers constituting 5 per cent of the crystals, whereas color, calcium, and sulphites are more uniformly distributed, the average percentage removals, obtained by Keane, Ambler, and Byall,¹ being as follows:

	Sugar	Color	Ash	SO ₃	SO ₂	CaO	Na ₂ O	K ₂ O	Cl	N
	%	%	%	%	%	%	%	%	%	%
I *.....	25.0	56.7	78.8	25.9	27.3	50.0	79.0	68.0
II †.....	13.4	20.5	58.4	63.7	29.5	76.0	66.3	88.3	60.9
III ‡.....	7.0	18.3	59.2	72.8	27.0	37.6	71.2	63.7	67.4	60.1

* Sugar removed 20.1 to 30%. † Sugar removed 10.1 to 20%. ‡ Sugar removed 10% and less.

Molasses.—The *U. S. Standards* specify for molasses not more than 25 per cent of moisture, also not less than 55 per cent of sugars (sucrose plus reducing sugars calculated as invert) in dark molasses and not less than 62 per cent in light molasses.

Investigations were undertaken by Van der Linden² with the view of deciding whether molasses is an undercooled eutectic mixture or a saturated solution of sucrose in non-sucrose solvent. Kalshoven³ continued the work and determined the fine grain, often present in molasses, by means of the refractometer. Since the purity regularly decreased with decreasing water content up to a certain point, he favors the view that molasses is a saturated solution of sucrose in non-sucrose solvent.

The composition of molasses, as analyzed at the sugar mills, is shown in several of the foregoing tables.

Typical samples of molasses from India sugar factories contained, as analyzed by Sen, Joshi, and Gupta,⁴ as follows:

¹ Ind. Eng. Chem. 1935, **27**, 30.

² Arch. Suikerind. 1919, **27**, 1511.

³ Ibid. 1919, **27**, 1560, 1663, 1967; 1920, **28**, 937.

⁴ J. Sci. Tech. India 1935, **1**, 53.

	Solids	pH	Total N	Red. sugars	Glucose	Gums	Ash, sulphate	Ash, carbonate
	%	%	%	%	%	%	%	%
Sulfitation...	77.	5.96	0.0087	15.09	2.66	1.43	12.34	9.36
Carbonated..	82.6	5.86	0.015	7.42	2.99	1.20	19.06	14.58
Gur refinery.	83.8	5.52	0.000	25.63	4.23	0.45	7.37	5.62

Analyses, reported by Browne,¹ of Cuban blackstrap molasses made through twenty years, show continual decrease of sucrose, irregular increase of invert sugar, decrease of total sugars after inversion, increase of organic non-sugars, and a decrease of about 3 per cent of total solids. The volatile acids were largely acetic and in small amount formic.

Frear,² in the examination of 14 samples of New Orleans molasses and 8 of other molasses from the market collected in 1912, found no conclusive evidence of adulteration with glucose sirup which in 1892 Wiley and co-workers showed was prevalent. The presence of sulphurous acid (SO₂) was due to the process of defecation. The minute amounts of zinc and tin detected appear to have been due to accidental contamination. In former years tin salts were used to give the product a light yellow color. A summary of Frear's results follows:

COMPOSITION OF MOLASSES (FREAR)

	Water	Sucrose	Red. sugars	Ash					SO ₃	SO ₂	Zinc	Tin
				Total	Sol.	Insol.	Alkalinity*					
							Sol.	Insol.				
	%	%	%	%	%	%	cc.	cc.	%	mg. per kilo	mg. per kilo	mg. per kilo
New Orleans:												
Min.....	19.80	23.52	14.46	3.95	3.23	0.68	0.80	1.44	0.29	0	0.0	0.0
Max.....	26.05	46.43	28.78	7.60	5.77	1.83	4.08	4.48	0.72	902	45.0	37.9†
Other kinds:												
Min.....	18.20	29.02	12.42	3.44	2.70	0.68	1.64	1.40	0.24	32	0.0	11.0
Max.....	26.15	47.85	23.08	7.58	6.34	2.36	4.38	5.22	0.54	188	35.3	44.1

* Cc. N/10 acid per 1 gram of molasses. † Contains some lead.

¹ Proc. Intern. Soc. Sugar Cane Tech. 1935, 5, 216.

² Pennsylvania Dept. Agr. Dairy and Food Div. 1912, Bul. 224, 61.

The higher percentage of sulphur in New Orleans molasses explains the characteristic lighter color of that grade as compared with the Puerto Rican product as formerly sold by retail grocers from the barrel.

McGill,¹ in the analysis of 140 samples of molasses sold in Canada, found: solids 70 to 80, sucrose 25 to 54, reducing sugars 10 to 37, and ash 1 to 9 per cent. Of these, 75 samples containing less than 40 per cent of sucrose were considered of low grade and hardly entitled to be sold for human consumption.

Hard Molasses, according to Schweizer and Van der Want,² as prepared in Java for use in the manufacture of arak, is black or dark green with a glassy fracture, and is very hygroscopic. Samples varied as follows: solids 92.4 to 96.3, glucose 25.4 to 34.7, ash 9.2 to 16.3 per cent, apparent purity 31.3 to 36.7, and true purity 38.0 to 43.7.

Influence of Soil on Composition.—Follett-Smith³ attributes to the higher alkali content of the soil the higher percentage of ash and alkalies in molasses from cane grown on the east coast of Demerara over that grown on the west coast, the figures reported being, respectively: ash (sulphated) 11.16 and 7.18 to 7.81, potash 3.19 and 1.66 to 1.78, soda 0.17 and 0.05 per cent.

Cane Sugar Sirup.—In Georgia and the Gulf States⁴ sirup is made directly from the cane juice by treatment with sulphur dioxide, liming to near neutrality, decolorizing, if dark, with carbon, further treatment with sodium phosphate, and concentration, at least in part, in an open kettle to develop a cooked taste.

The *U. S. Standards* define sirup as being made by the purification and evaporation of the juice of a sugar-producing plant without removal of any of the sugar. In sugar-cane sirup, which may also be made by the solution of the concrete, water is limited to 30 per cent and ash to 2.5 per cent.

Sugar sirup, made by dissolving sugar, is not allowed to contain more than 35 per cent of water.

CONSTITUENTS.—See also Introduction to Part I.

Proteins.—See results by Browne and Blouin above.

Amino Acids.—Shorey⁵ isolated *leucine* and *glycocoll* from cane

¹ Inland Rev. Dept., Ottawa, Canada, Bul. 312.

² Arch. Suikerind. 1916, 24, 597.

³ Brit. Guiana Dept. Agr. Div. Rep. 1934, 1932, 106.

⁴ U. S. Dept. Agr. Bul. 1370. See also Horne: loc. cit.

⁵ J. Am. Chem. Soc. 1897, 19, 881; 1898, 20, 133.

juice, but the presence of glycocoll has been questioned by Campaigne¹ and Zerban.² Zerban isolated *tyrosine*.

Purine Bases.—Shorey³ isolated *guanine* from the juice of Hawaiian cane.

Choline Bases.—Shorey⁴ obtained a small amount of *lecithin* in the juice and noted the probable presence of *betaine* and *choline* derived from lecithin.

Amides.—Maxwell⁵ isolated *asparagine* from cane juice. Zerban, noting that Maxwell did not identify his preparation by physical and chemical tests, separated the substance and established its identity. He also isolated and identified *glutamine*.

Acids.—*Aconitic acid* occurs in cane juice, as was first announced by Behr.⁶ This acid occurs also in cane molasses together with other acids, notably *formic*, *acetic*, and *lactic*, which are formed during the process of manufacture. The last two are believed to result from the action on sucrose of the lime used in defecation.

P. A. Yoder⁷ determined the acids in the juice of a mixture of four varieties of cane with results as follows: sulphuric acid (SO_3) in part 0.00051, phosphoric acid (P_2O_5) 0.00314, *oxalic acid* 0.00004, tartaric acid 0, *malic acid* 0.00077, succinic acid 0, aconitic acid about 0.05, and citric acid 0 per cent.

Nelson⁸ found in cane molasses: formic acid about 0.1, acetic acid 0.2, aconitic acid 0.8, lactic acid 0.05 per cent, and small quantities of malic and citric acids. *Citric acid* had not previously been reported as a constituent of cane molasses.

Zerban⁹ secured the following percentages of *formic acid* in cane products, the figures in parentheses being the number of samples: raw sugar (6) 0.004 to 0.027, aver. **0.010**; molasses (1) 0.004; final molasses (2) 0.139, 0.154; sirup (7) 0.007 to 0.015, aver. **0.011**; soft refinery sugar (15) 0.014 to 0.155, aver. **0.08**, refined sugar trace; filtered refinery sirup (2) 0.791, 0.678; final refinery molasses (2) 0.586, 0.416 per cent.

¹ Arch. Java Suikerind. 1899, p. 751.

² 8th Int. Cong. Appl. Chem. 1912, **8**, 103.

³ J. Am. Chem. Soc. 1899, **21**, 809.

⁴ Ibid. 1898, **20**, 133.

⁵ Louisiana Agr. Exp. Sta. 1895, Bul. **38**, 1380.

⁶ Ber. 1877, **10**, 351.

⁷ J. Ind. Eng. Chem. 1911, **3**, 640.

⁸ J. Am. Chem. Soc. 1929, **51**, 2808.

⁹ J. Ass. Off. Agr. Chem. 1932, **15**, 355.

Carbohydrates. *Sucrose, Dextrose, Levulose, Invert Sugar.*—See Introduction to Part I and foregoing tables.

Glucose.—Geerligs¹ observed that in the analysis of cane sugar there is a wide discrepancy between the sum of the determinable constituents and 100, due he believed to the decomposition products of invert sugar which have low reducing and rotatory power and are partly precipitated by basic lead acetate. This observation is confirmed by the work of Muller,² Pellet and Muller,³ and Pellet,⁴ who show that cane molasses contains glucose and that the methods previously in vogue give erroneous results. In 9 samples Muller found 3.20 to 4.96 per cent of glucose, whereas in 2 samples of beet molasses he found only 0.10 to 0.16 per cent. Pellet⁵ gives figures for glucose ranging from 2.6 to 5.6 per cent. This sugar is non-fermentable, has a reducing power only half that of invert sugar, and is optically inactive.

See also Sen, Joshi, and Gupta above.

Colors.—Sakuma and Momose⁶ identified an *anthocyanin* and *tannin* as the pigments of red and purple cane and reached the conclusion that the iron-tannin compound of cane juice is an amethyst-colored pigment. Lignin, saccharetin, numerous colors formed by the action of hydrochloric acid and lime water, and the red rot disease were also studied.

Mineral Constituents.—The data given in the following table were compiled from results published by Browne and Blouin⁷ and by Spencer.⁸ Those credited to Hall are included in Browne and Blouin's Bulletin. It should be noted that the composition of molasses cannot be predicted from the composition of the juice, since defecation adds certain mineral constituents and removes others, the amounts in both cases depending on the details of treatment.

Figures on phosphoric acid and sulphuric acid are given above in the table of minor constituents under white sugar.

Experiments by Zerban⁹ gave the following amounts of sulphur as sulphurous acid in the products from sulphurized juice, expressed on

¹ Intern. Sugar J. 1910, **12**, 293, 332.

² Arch. Suikerind. 1917, **25**, 352; 1918, **26**, 346.

³ Bul. ass. chim. suc. dist. 1917, **35**, 116.

⁴ Ibid. 1917, **35**, 118.

⁵ Ann. chim. anal. 1917, **22**, 43.

⁶ J. Soc. Chem. Ind. Japan 1935, **38**, Suppl. bind. 161, 224, 225, 227, 293.

⁷ Louisiana Agr. Exp. Sta. 1907, Bul. **91**, 4, 27, 92.

⁸ Handbook for Cane-Sugar Manufacturers and Their Chemists, New York, 1917, p. 8.

⁹ Sugar Planters' J. 1907, **37**, 314.

COMPOSITION OF THE ASH OF SUGAR-CANE PRODUCTS

	K ₂ O	Na ₂ O	CaO	MgO	Fe ₂ O ₃	Al ₂ O ₃	P ₂ O ₅	SO ₃	SiO ₂	CO ₂	Cl	C
	%	%	%	%	%	%	%	%	%	%	%	%
Leaves (Hall).....	31.25	1.17	5.90	5.11	1.45	1.03	7.25	11.29	30.32	1.10	3.08	0.16
Stalk (Hall).....	38.23	1.30	5.19	5.76	1.13	0.25	5.27	18.47	15.70	2.70	4.52	0.54
Juice (Hall):												
Min.....	40.66	0.63	3.00	3.21	0.45	0.18	5.31	20.40	4.80	3.30	3.26
Max.....	49.63	1.81	4.62	7.45	1.48	1.25	6.38	23.69	9.30	4.10	5.83
Juice (Spencer):												
Min.....	25.15	1.36	4.70	5.01	3.00		tr.	4.08	5.56	2.68	5.10
Max.....	46.28	5.35	13.02	7.88	19.00		7.15	17.94	11.90	10.53	12.90
Molasses (B. and B.):												
Sulphitation												
Mill.....	49.48	0.89	6.47	4.29	0.35	0.30	3.71	10.79	4.12	7.49	14.00
Diffusion.....	52.20	0.80	6.78	3.09	0.33	0.22	3.80	6.72	4.59	11.19	11.95
Open kettle.....	51.48	1.11	6.58	3.99	0.15	0.13	2.12	10.94	2.83	13.06	9.10
Carbonatation.....	50.16	0.32	8.53	2.66	0.47	0.30	0.91	11.18	4.10	15.78	4.59

the basis of 100 parts added: clarified 30, sirup 17.24, first massecuite 10.86, first molasses 8.77, second massecuite 7.76, second massecuite after four weeks in hot room 2.97, second molasses 2.21, third massecuite 1.89. In raw sugar the sulphur dioxide ranged from 0.006 to 0.0195 per cent and the total sulphur from 0.0653 to 0.4267 per cent.

Egyptian cane molasses, examined by Von Lippmann,¹ on charring and extraction with water yielded an insoluble residue containing 0.66 per cent of titanium, an element known to be abundant in the silt of the Nile.

Minor Mineral Constituents. *Iron.*—Molasses 79.7 mg. per kilo, fresh basis (Peterson and Elvehjem).² Granulated sugar 0.6 to 1.0, aver. 0.9 mg. per kilo (Toscani and Reznikoff).³

Manganese.—Molasses 5.5 mg. per kilo, dry basis (Peterson and Skinner).⁴

Copper.—Molasses 19.3 mg. per kilo, fresh basis (Lindow, Elvehjem, and Peterson).⁵

¹ Ber. 1925, 58B, 426.

² J. Biol. Chem. 1928, 78, 215.

³ J. Nutrition 1934, 7, 79.

⁴ Ibid. 1931, 4, 419.

⁵ J. Biol. Chem. 1929, 82, 465.

SORGHUM PRODUCTS

IN parts of the United States sirup has long been made from the stalks of sugar sorghum (*Andropogon Sorghum* (L.) Brot. var. *saccharatus* Körn). Sherwood ¹ states that 49,505,000 gallons were made during the year 1920. Collier, during his connection with the United States Department of Agriculture, conducted extensive experiments on the production of white sugar from sorghum, but without practical results.

Sorghum Sirup.—Sherwood ¹ analyzed the juice of 15 varieties of sugar sorghum, noting especially the influence of starch on the process of manufacture. A summary of his results follows:

COMPOSITION OF SUGAR SORGHUM JUICE (SHERWOOD)

	Sp. gr. 17.5° C.	Sucrose (A)	Reducing sugar * (B)	Starch (C)	$\frac{B + C}{A}$
		%	%	%	
Minimum.....	1.0564	6.86	0.60	0.142	0.11
Maximum.....	1.0900	15.75	5.99	0.852	0.73
Average.....	1.0724	11.33	2.65	0.366	0.30

* Calculated as invert.

He considers that starch is largely responsible for the difficulty of filtering the juice and the jellying of the sirup, although it probably tends to retard crystallization. Preliminary treatment with malt diastase hastens the filtration and prevents jellying.

Willaman and Davison ² conclude from their studies that the alcohol precipitate from sorghum sirup, exclusive of occluded material, is largely starch, but some true gum containing galactan is also present.

An analysis of sorghum sirup by Jordan and Chesley ³ follows:

¹ Ind. Eng. Chem. 1923, 15, 727, 781.

² Ibid. 1924, 16, 609.

³ Ibid. 1917, 9, 756.

COMPOSITION OF SORGHUM SIRUP (JORDAN AND CHESLEY)

Solids	Sucrose	Reducing sugars	Gums and extractives	Acidity as tartaric	Ash
% 74.63	% 40.00	% 28.42	% 4.03	% 0.79	% 2.82

The *U. S. Standards* limit water in sorghum sirup to 30 per cent and ash to 2.5 per cent.

Color.—Willaman and Easter¹ have studied the factors affecting the color of the sirup. They employ the Pfund color grader, calibrating the color glass wedge against a spectrophotometer.

Mineral Constituents.—Refuting the claim that sirup from sorghum grown in the arid regions contains an excess of mineral matter, Vinson and Catlin² give an analysis of a sample from cane grown near Yuma showing a relatively low ash content.

¹ Ibid. 1929, 21, 1138.

² Arizona Agr. Exp. Sta. Rep. 1916, p. 301.

CORN STALK PRODUCTS

ACCORDING to Willaman, Burr, and Davison,¹ the juice of the stalks of sweet corn is not a profitable source of white sugar because of the low purity, but may be utilized for sirup manufacture. By removing the ears at the canning stage and cutting ten to twenty days thereafter the yield is increased. Naudain² states that the juice of sweet corn cobs contains sugar that may be utilized, after removal of the tannin by decolorizing carbon and other agents. See also reference to corn stalks as a source of sugar in the Introduction to Part I.

¹ Ind. Eng. Chem. 1924, **16**, 734.

² Am. Food J. 1925, **20**, 508.

PALM STALK PRODUCTS

Nipa Palm Sugar.—Gibbs ¹ suggests that the sap of the nipa palm (*Nipa fruticans* Wurmb.), long used by Philippine natives for the production of beverages and vinegar, be utilized as a source of commercial sugar. His analyses of the sap show approximately: specific gravity at 15° C. 1.0720, solids 18.0, sucrose 17.0, reducing sugars trace, acid trace, and ash 0.48 gram per 100 cc. Roxas ² under favorable conditions obtained juice with an average polarization of 12.58 and recovered 40.67 per cent of commercial sugar. Owing to the presence of 0.37 per cent of sodium chloride in the juice, the sugar contained 0.2 to 0.5 per cent of this impurity. Others who have written on the possibility of nipa palm sugar are Reijgersbergh ³ and Dennett.⁴

Date Palm Sugar.—Annet ⁵ among others conducted experiments on the manufacture of sugar from the date palm (*Phoenix dactylifera* L.). Experiments on the production of sirup were carried out by Roy.⁶

Sugar Palm Sugar.—Milsum and Dennett ⁷ describe the production of sugar from *Arenga saccharifera*. Although the juice of 2 samples contained only 4.89 and 7.10 grams per 100 cc. of sucrose, the purity was high.

Palmyra Palm Sugar.—Ghose ⁸ calls attention to sugar made in the Province of Bihar, India, from the palmyra palm (*Borassus flabellifer* L.). A daily production per tree of 5 to 7 kilos of juice, containing 12.5 per cent of sucrose, is not unusual.

¹ Philippine J. Sci. 1911, 6, 99.

² Ibid. 1929, 40, 185.

³ Arch. Suikerind. 1925, 33, 1244.

⁴ Malayan Agr. J. 1926, 14, 375.

⁵ Agr. J. India 1917, 12, 442.

⁶ Ann. Rept. Dept. Agr. Bengal 1927, Year 1925-26, 40.

⁷ Malayan Agr. J. 1929, 17, 449.

⁸ Agr. J. India 1920, 15, 72.

SUGAR BEET PRODUCTS

THE structure and composition of sugar beets and beet juice are considered in Volume II. It remains to give data on the composition of raw and refined beet sugar and beet molasses, dwelling especially on impurities such as amino acids, betaine, choline, raffinose, etc.

Manufacture of Beet Sugar.—The diffusion process is now almost exclusively employed. In general this process consists of six stages: (1) cutting, (2) diffusion of the juice, (3) defecation, (4) evaporation, (5) crystallization, and (6) centrifuging, the chief difference from the process used in cane sugar manufacture being in the extraction of the juice, which is not expressed but is soaked out by water from the sliced beets (*cossettes*) at 80° C. or somewhat higher. The hot water coagulates and ruptures the protoplasmic film on the cell walls, facilitating the diffusion.

For defecation, calcium hydroxide, followed by the removal of the excess with carbonic acid (carbonatation), is employed. A second defecation after evaporation to a sirup is also practiced. Sulphitation, after the second defecation, is employed if white sugar is made without refining with bone black.

In Russia and western Europe, beet juice is separately limed and carbonated, but sulphuring of the thin juice is omitted. Nevertheless, according to Kagnaer and Loginov,¹ the final purity of the thick juice is practically the same as that obtained by the American process of simultaneous liming and carbonatation followed by sulphuring.

MICROSCOPIC STRUCTURE.—Honig² calls attention to the value of microscopic examination in sugar manufacture. For example, careless washing of the pan to remove false grain causes irregular growth, splitting of the crystals, and formation of pockets. High-pressure steam in the centrifuge may burst or distort the crystals, and certain suspended particles, but not ultramarine as commonly supposed, are seen to form nuclei for sugar crystals.

¹ Trudui Zavodskikh Gruppovuih Lab. Sakhar. Zavodov (Voronezh. Sakharosveklotrest.) 1935, No. 2, p. 10.

² Arch. Suikerind. 1927, 35, 693.

According to Kryz,¹ beet molasses shows clusters of raffinose needles and octahedral inorganic crystals, whereas cane molasses contains fine single needles, cell fragments, and drops of a dark brown liquid insoluble in the molasses. The microscope also shows quickly the fineness of the sugar.

CHEMICAL COMPOSITION. Juice.—See Beet Root, Volume II.

Illustrative of the detailed chemical control exercised over beet sugar products are the average figures for the years 1935 and 1936 on diffusion juices from 19 Polish sugar factories compiled by Vondrák and Kmínek² as follows: sugar 18.49 per cent, polarization 16.92, quotient 91.52, non-sugars 9.28 per cent, "0.1 N ash as sulphate" 2.19 per cent. The following are in parts per 100 parts of polarizable sugar: total nitrogen 0.576, albumin nitrogen 0.075, ammonia nitrogen 0.031, amino nitrogen 0.140, betaine nitrogen 0.176, injurious nitrogen 0.403, potash 0.674, soda 0.082, and phosphoric acid 0.239.

Kmínek, also Vondrák and Kmínek,³ have given special attention to the nitrogen of diffusion sugar beet juices detrimental in sugar manufacture. Calculated on the basis of 100 parts of polarizing sugar, the values were: albumin nitrogen 0.076, ammonia nitrogen 0.025, amino acid nitrogen 0.146, betaine nitrogen 0.139, "detrimental nitrogen" (sum of foregoing) 0.385, and total nitrogen 0.558 per cent.

The extensive literature on the composition of beet juice is of interest chiefly to producers. The following brief abstracts suffice for this work.

Raw Sugar.—Fischek⁴ gives the average annual composition of the raw sugar, received at a Bohemian factory from 1900 to 1907 inclusive, of which the following is a summary:

COMPOSITION OF RAW BEET SUGAR (FISCHEK)

	Polarization *	Water	Organic non-sucrose	Yield white sugar	Yield molasses
	°V	%	%	%	%
Minimum	94.57	1.89	1.72	88.76	5.47
Maximum	95.16	2.42	2.16	89.50	10.58

* In degrees representing percentages of sucrose.

¹ Z. Zuckerind. czechoslov. Rep. 1925, **49**, 295.

² Listy Cukrovar. 1936, **55**, 57.

³ Ibid. 1935, **54**, 29.

⁴ Z. Zuckerind. Böhmen 1908, **32**, 499

Refined Sugar.—Beet sugar, after careful refining, differs in no essential detail from cane sugar, and the two products are sold interchangeably as sugar.

The minor impurities found by Byall and co-workers are tabulated under cane sugar. De Whalley,¹ refuting the claim that the best British beet sugar contains 2 per cent of raffinose, states that it consists of 99.95 per cent of sucrose together with not more than 0.02 per cent water, 0.01 per cent of ash, and 0.02 per cent of organic non-sugars.

Molasses.—Beet molasses differs materially from cane molasses in composition and is not suited for human food. It is not relished by farm animals, but is well adapted for alcohol production, and the residue, being rich in nitrogen and mineral salts, for use as a fertilizer.

Kolar² gives the following analyses of massecuites and final molasses obtained by the Karlik-Czapikowski process:

COMPOSITION OF BEET MASSECUITE AND MOLASSES (KOLAR)

	Brix *	Water	Org. matter	Sucrose	Ash	Purity coeff.	Saline coeff.	Org. matter ash
		%	%	%	%	%	%	%
1st massecuite....	94.42	5.58	4.08	88.60	1.74	93.90	50.10	2.54
2nd massecuite....	91.35	8.35	12.36	73.80	5.19	80.79	14.22	2.38
Molasses.....	83.69	15.31	23.01	51.90	9.78	62.00	5.30	2.35

* Graduation of the Brix hydrometer is in percentages of sucrose.

Analyses by Meyer³ of molasses from two American factories, one in California and the other in Colorado, using Steffen's process, are given below; ash analyses appear in a subsequent section.

COMPOSITION OF AMERICAN BEET MOLASSES (MEYER)

	Water	Protein N $\times 6\frac{1}{4}$	Suc- rose*	Invert sugar	Raf- finose	Alka- linity	Car- amel	Vol. acids	Glu- tamic acid	Be- taine	Pen- toses
	%	%	%	%	%	%	%	%	%	%	%
California....	17.80	17.69	50.59	0.10	0.11	0.14	1.49	1.92	3.10	2.22	0.51
Colorado....	23.19	15.19	46.70	0.17	3.51	0.09	0.90	3.54	2.40	2.56	0.56

* Raffinose formula; Clerget formula gave 50.65, 49.0%. Direct polarization 50.8, 53.2; invert polarization —16.4, —12.0.

¹ Food, 1933, 3, 26.

² Z. Zuckerind. Böhmen 1910, 34, 525.

³ Z. Ver. Zuckerind. 1909, 59, II, 1019.

Saillard¹ attacks as invalid the method of calculating the loss of sucrose in molasses by the Andrlík coefficient. During growth the total nitrogen-sugar ratios decrease, the albuminoid nitrogen-total nitrogen ratios increase, and the content of ammoniacal, amide, and harmful nitrogen decreases. The molasses contains a small amount of albuminoid nitrogen.

CONSTITUENTS.—See also Introduction to Part I.

Proteins.—Little is known about the true proteins present in beet juice and molasses and as impurities in raw and refined sugar.

Amino Acids.—Staněk² devised a method for determining *l*-glutamic acid in sugar house products. By this method he found in beet molasses 5 to 7.8 per cent during 1910–11 and 3 to 4.7 per cent during 1911–12. Andrlík³ improved a method of preparation, previously devised by him, securing glutamic acid in addition to pure betaine. Parisi,⁴ who makes flattering mention of the results of Ravenna⁵ on nitrogen distribution in beet molasses, has devised a scheme for separation of amino acids, also betaine. The amino acids thus separated are *leucine*, *tyrosine*, *arginine*, *lysine*, and *histidine*.

Choline Bases.—*Betaine* has long been known to be a constituent of beet molasses. Stolzenberg⁶ criticizes the method of preparation of betaine devised by Urban.⁷ Andrlík, as noted below, obtained pure betaine. Staněk⁸ isolated *choline* from beet molasses, taking advantage of its precipitation in an alkaline solution, whereas betaine is precipitated only in an acid solution. Parisi, as noted above, separates betaine, in addition to the amino acids, in his scheme.

Davies and Dowden⁹ state that *betaine* makes up 38 per cent of the soluble nitrogen in molasses and molasses beet pulp. The latter contains also 0.1 per cent of *trimethylamine oxide*, which, being five to eight times that in the molasses, indicates decomposition of the betaine during drying.

Nitrates.—Pellet and Müller,¹⁰ by a modification of Boussingault's method, found in beet molasses 0.5 per cent of nitric nitrogen calculated as KNO_3 .

¹ Pub. inst. belge amelioration betterave 1936, 4, 251.

² Z. Zuckerind. Böhmen 1915, 39, 191.

³ Ibid. 1915, 39, 387.

⁴ Ann. chim. applicata 1925, 15, 555.

⁵ Ann. soc. agr. prov. Bologna 1912, 62, 157.

⁶ Zentr. Zuckerind. 1914, 22, Nos. 4 and 5.

⁷ Wochschr. Zentralver. Rübenzucker-ind. 1913, 51, 315.

⁸ Listy Cukrovar. 1930, 49, 135.

⁹ J. Soc. Chem. Ind. 1936, 55, 175T.

¹⁰ Intern Sugar J. 1911, 13, 493.

Acids.—In addition to the acids present in beet juice (see Beet, Volume II), molasses is stated by Ehrlich¹ to contain *acetic*, *formic*, and *butyric acids*. According to Smolensky,² *lactic acid* is formed in molasses by fermentation. In the residual molasses of a Gregorowka refinery he isolated *magnesium lactate* as a white, partly crystalline powder. Zerban³ obtained 0.040 per cent of *formic acid* in a single sample of raw beet sugar.

Nakhmanovich and Berman⁴ have shown that the total amount of *pectic acid* increases during growth, but that soluble in water at 80° C. decreases. There is no difference in the amount extracted at different degrees of acidity (*pH* 3.3 to 6.6), but in alkaline solution (*pH* 11.2 to 11.4) the solubility is greater than in acid.

Carbohydrates. *Sucrose, Invert Sugar.*—See Introduction to Part I and foregoing tables.

The results of an experiment by Pázler⁵ show that early-planted beets yield higher percentages of sucrose (maximum 19.46) and lower percentages of injurious amino acids than late-planted beets.

Raffinose.—The occurrence of raffinose, its influence on polarimetric sugar determination, yield in refining, and other problems involving this sugar have been subjects of much controversy. A conference held in Berlin in 1910 considered some of these problems.⁶ Molenda⁷ claims that the material reported in crude sugar is not raffinose or even a sugar. Experiments by Schecker⁸ indicate that even the maximum of 4.5 per cent of raffinose commonly present in beet molasses has only a slight effect on yield. Mehrle⁹ states that some raffinose and ash are deposited in the sucrose crystals, other organic impurities only on the surface. Schecker,¹⁰ however, believes that this is true only under certain conditions. Zitowski¹¹ endorses Herzfeld's view that raffinose is formed in the beet by the action of frost.

Pentosans.—Appreciable amounts of pentosans have been noted by several authors. The results of studies by Pellet¹² throw doubt on the

¹ Chem.-Ztg. 1911, **35**, 661.

² Centr. Zuckerind. 1919, **18**, 1427.

³ J. Ass. Off. Agr. Chem. 1932, **15**, 355.

⁴ Bul. ass. chim. 1936, **53**, 872.

⁵ Listy Cukrovar. 1936 **55**, 41.

⁶ Deut. Zuckerind. 1910, **35**, 687; 1911, **36**, 203.

⁷ Oesterr. Ung. Z. Zuckerind. 1914, **43**, 48, 232.

⁸ Z. Ver. deut. Zuckerind. 1924, **74**, 83.

⁹ Deut. Zuckerind. 1925, **50**, 1357.

¹⁰ Ibid. p. 1413.

¹¹ Am. Sugar. Ind. 1911, **13**, 260.

¹² Bul. ass. chim. suc. dist. 1917, **35**, 117.

presence of true pentosans in beet molasses and indicate that the amount of substances related to them is very small, not exceeding 0.2 per cent.

Brodowski¹ estimated that the beet molasses examined by him contained 1.07 per cent of colloids, of which 0.69 per cent was reversible. One of the reversible colloids was *araban*. Of the fractions yielded by the irreversible colloids, three were acid and three amphoteric.

Colors.—According to Stolzenberg² two coloring substances occur in molasses: (1) a fluorescent, hygroscopic acid obtained as a partly resinous and partly crystalline white mass, readily soluble in alcohol, and (2) a brown-black substance containing 6.6 per cent of nitrogen, insoluble in alcohol but soluble in alkalis, reprecipitated by acid, and precipitated by lead acetate; it is judged to contain HO groups and basic nitrogen and to have a carbon nucleus of cyclic structure.

Staněk³ also isolated a dark-colored pigment, apparently identical with that of Stolzenberg, which somewhat resembled *fuscazinic acid* and was regarded as a condensation product of amino acids and sugar. Friedrich⁴ in the main agrees with Staněk but considers that the amino acids condense with caramel rather than sugars. Pollak and Knob⁵ state that the color is due to compounds of the humic acid type.

Garino, Regè, and Rubino⁶ refer to two types of color: (1) formed by the caramelization process and (2) formed by the action of lime on the invert sugar.

Mineral Constituents.—In diffusion beet juices, calculated on the basis of 100 parts of polarizing sugar, Vondrák and Kmínek⁷ found potash (K_2O) 0.710, soda (Na_2O) 0.078, and phosphoric acid (P_2O_5) 0.231.

Von Stietz,⁸ who was engaged in devising a suitable method of burning molasses under the boilers of the sugar factory, gives the following range in composition:

¹ Kolloid-chem. Beihefte 1929, **29**, 261.

² Ber. 1916, **49**, 2021.

³ Z. Zuckerind. Böhmen 1917, **41**, 298, 607, 618.

⁴ Ibid. 1917, **41**, 614.

⁵ Brennerei-Ztg. 1922, **39**, 39.

⁶ Giorn. chim. ind. appl. 1929, **11**, 61.

⁷ Loc. cit.

⁸ Arch. Suikerind. 1920, **28**, 519.

COMPOSITION OF BEET MOLASSES ASH (VON STIETZ)

	Ash	Insol. in water	K ₂ O	Na ₂ O	CaO	MgO	SO ₃	SiO ₂	Cl	Calcium and iron phosphates
	%	%	%	%	%	%	%	%	%	%
Min.	7	15	30	0	1	1	6	1	3	4
Max.	12	30	50	1	10	2	15	5	10	15

By spectroscopic examination Von Lippmann¹ detected *lithium* and *scandium* in Canadian beet molasses.

Pellet² states that the *sulphur dioxide*, introduced for defecation, oxidizes during the subsequent processes and occurs only in traces or not at all in the molasses.

¹ Ber. 1925, 58B, 426.
² Bul. ass. chim. suc. dist. 1907, 24, 749.

MAPLE PRODUCTS

Maple Sap.—The sap of the maple tree furnishes two distinctively American and Canadian foods, maple sirup and maple sugar, both characterized by their peculiarly delicious flavor. The species ordinarily furnishing the sap is *Acer saccharum* Marsh. or its variety *nigrum* Brit. The season of production is limited to six weeks or two months in the Spring. The trees are tapped by boring holes $\frac{3}{8}$ to $\frac{1}{2}$ inch in diameter and $1\frac{1}{2}$ to 2 inches deep, into each of which is inserted a combined spout and hook for suspending the pail to collect the sap.

Manufacture of Maple Sirup and Maple Sugar.—The process consists in boiling down the sap to the proper density, skimming off the scum containing proteins which would cause fermentation, and removing the deposit consisting chiefly of calcium malate, known as “niter,” “sugar sand,” or “silica,” by settling or straining through flannel.

In the preparation of the sirup, the concentration of the sap is continued until a gallon weighs 11 pounds (solids 65 per cent, water 35 per cent), as indicated by the boiling point of 219° F. (104° C.) following the plan of the Vermont Agricultural Experiment Station or by the density 35.6 Bé. at 60° F. (16° C.). If the concentration is continued until the boiling point of 233 to 250° F. (112 to 121° C.) is reached the mass may be “sugared off,” that is, converted into maple sugar of different degrees of hardness on cooling.¹ Much of the sirup on the market is prepared by dissolving maple sugar.

Statistics of Production.—According to census reports 4,106,418 gallons of maple sirup and 14,060,206 pounds of maple sugar were produced in the United States in the year 1910, the total money value of the products being \$5,177,809, or by states as follows: New York \$1,240,684, Ohio \$1,099,248, Vermont \$1,086,933, Pennsylvania \$417,213, Michigan \$333,791, Indiana \$300,755, and New Hampshire \$182,341.¹ The Province of Quebec census of 1911 places the value of the maple sirup and sugar produced in that province at \$1,680,000, or

¹ Bryan and Hubbard; U. S. Dept. Agr. 1912, Farm Bul. 516.

nearly as much as of poultry and more than of sheep, cream, or fruits.¹

Definitions and Standards.—The following definitions appear in the announcement of the U. S. Secretary of Agriculture, May 11, 1932:

Maple sugar, maple concrete, is the solid product resulting from the evaporation of maple sap or maple sirup.

Maple sirup is sirup made by the evaporation of maple sap or by the solution of maple concrete, and contains not more than 35 per cent of water, and weighs not less than 11 pounds to the gallon (231 cubic inches).

McGill² recommends the following standards: maple sugar should contain not more than 10 per cent of water and, on the dry basis, not less than 0.60 per cent of ash in carbonate condition, 0.12 per cent of ash insoluble in water, and 0.30 per cent of malic acid; it should have a Canadian lead number of not less than 1.7 and Winton lead number of not less than 1.2. Maple sirup should have not over 35 per cent of water, and the dry substance should be similar to that of maple sugar. These standards are reviewed by Snell.³

CHEMICAL COMPOSITION.—The cane and beet sugar refiner produces commercial sucrose of the highest degree of purity; the manufacturer of maple sirup and maple sugar, however, strives to retain certain impurities, realizing that the epicurean, and consequently market, value of his products depends on the flavoring constituents contained therein. It is accordingly obvious that determinations of sucrose and invert sugar, such as those by Bryan⁴ and Bryan, Straughn, Church, Given, and Sherwood,⁵ given in the first of the three following tables, while showing the dietetic value, furnish few data applicable in distinguishing maple sirup and maple sugar from readily prepared imitations. Although the tabulated figures on the sirups are on the wet basis and are not strictly comparable with those on the sugars, which are on the dry basis, it can be seen at a glance that the difference between the two products, aside from moisture content, lies chiefly in the tendency toward a higher percentage of invert sugar in the maple sugar due to the longer boiling and greater concentration.

Of the other two tables, one summarizes by states results by Bryan and collaborators on the total, soluble, and insoluble ash, lead number, and malic acid number; the other table summarizes results of several

¹ Snell: J. Soc. Chem. Ind. 1914, **33**, 507.

² Inland Rev. Dept., Ottawa, Canada 1911, Bul. **228**.

³ J. Soc. Chem. Ind. 1914, **33**, 507.

⁴ U. S. Dept. Agr., Bur. Chem. 1910, Bul. **134**.

⁵ U. S. Dept. Agr. 1917, Bul. **466**.

analysts on these constituents and also on the alkalinity of the ash and electrical conductivity as compiled by Snell and Scott.¹ The figures in both tables are of little interest to the dietitian but are specially designed to aid the analyst in detecting the admixture of refined sugar or other saccharine adulterants.

COMPOSITION OF MAPLE PRODUCTS (BRYAN ET AL.)

Maple Sirup (As sold)							Maple Sugar (Dry basis)				
	Samples	Water	Suc-rose	Invert sugar	Ash	Unde-termined	Samples	Suc-rose	Invert sugar	Ash	Unde-termined
United States:	395	%	%	%	%	%	283	%	%	%	%
Min.....		24.85	47.20	0.17	0.46	0.00		57.04	0.09	0.76	0.00
Max.....		48.14	70.46	10.23	1.06	4.51		98.62	37.30	1.66	5.84
Aver.....		34.19	62.64	1.49	0.66	1.02		91.89	5.46	0.95	1.70
Canada:	86						80				
Min.....		30.58	48.34	0.00	0.45	0.00		58.92	0.88	0.76	0.02
Max.....		42.88	67.29	11.01	0.90	3.28		96.59	35.26	1.70	8.18
Aver.....		34.34	62.24	1.41	0.62	1.59		86.48	8.76	1.06	3.70
Both countries:	481						363				
Min.....		24.85	47.20	0.00	0.46	0.00		57.04	0.09	0.76	0.00
Max.....		48.14	70.46	11.01	1.06	4.51		98.62	37.30	1.70	8.18
Aver.....		34.22	62.57	1.47	0.66	1.08		90.69	6.19	0.98	2.14

Tobey ² gives the following range in composition of 13 samples of maple sugar and 32 samples of maple sirup respectively: sucrose 89.3 to 96.2 and 47.4 to 65.2 per cent; ash 0.74 to 0.99 and 0.48 to 0.93 per cent; lead number 1.71 to 3.35 and 0.94 to 2.4. He gives as minimum limits for maple sugar: ash 0.65 per cent and lead number 1.83, dry basis. Maple sirup should contain not more than 35 per cent of water and not less than 0.45 per cent of ash, and should have a lead number of not less than 1.19.

Refined sugar, the commonest adulterant, contains practically no ash, no malic acid, and no substances forming a precipitate with lead subacetate, the reagent used in determining the lead number. Raw and brown sugar are seldom, if ever, used since they would injure the flavor.

The Canadian and Winton *lead numbers*, also the *malic acid number*, are determined by conventional methods which must be strictly

¹ J. Ind. Eng. Chem. 1914, 6, 216.
² Maine Agr. Exp. Sta. 1936, Off. Inspec. Bul. 159, 6.

ASH, LEAD NUMBER, AND MALIC ACID NUMBER OF MAPLE PRODUCTS (BRYAN ET AL.)

(Results calculated to dry basis)

Maple Sirup							Maple Sugar					
	Sam- ples	Ash			Win- ton lead No.*	Malic acid No.†	Sam- ples	Ash			Win- ton lead No.*	Malic acid No.†
		Total	Sol.	Insol.				Total	Sol.	Insol.		
		%	%	%				%	%	%		
Indiana:	23						19					
Min.....		0.87	0.46	0.23	1.91	0.85		0.84	0.60	0.23	2.17	0.76
Max.....		1.68	0.84	0.97	4.05	1.75		1.58	1.06	0.77	4.43	1.27
Aver.....		1.16	0.68	0.48	3.00	1.20		1.08	0.72	0.36	3.04	1.00
Maine:	9						4					
Min.....		0.90	0.59	0.24	1.76	0.31		0.78	0.55	0.23	2.08	0.65
Max.....		1.35	0.77	0.72	3.18	1.48		0.96	0.65	0.34	2.81	0.99
Aver.....		1.09	0.66	0.43	2.33	0.94		0.90	0.61	0.29	2.43	0.82
Maryland:							11					
Min.....			0.78	0.44	0.23	2.13	0.62
Max.....			1.13	0.77	0.41	3.23	1.08
Aver.....			0.91	0.60	0.31	2.61	0.85
Massachusetts:	10						14					
Min.....		0.81	0.50	0.23	1.85	0.68		0.87	0.61	0.23	2.17	0.76
Max.....		1.27	0.80	0.47	3.19	1.32		1.09	0.79	0.34	3.29	1.10
Aver.....		0.95	0.64	0.31	2.46	0.96		0.98	0.72	0.26	2.67	0.99
Michigan:	23						23					
Min.....		0.81	0.50	0.23	1.88	0.79		0.77	0.46	0.22	1.91	0.60
Max.....		1.61	1.23	0.68	3.55	1.44		1.10	0.78	0.43	3.29	1.15
Aver.....		0.99	0.63	0.36	2.60	1.00		0.90	0.62	0.28	2.52	0.83
New Hampshire:	15						12					
Min.....		0.68	0.41	0.26	1.88	0.66		0.80	0.48	0.25	1.91	0.72
Max.....		1.04	0.81	0.44	3.46	1.27		1.13	0.74	0.43	3.48	1.21
Aver.....		0.94	0.55	0.39	2.63	0.98		0.91	0.59	0.32	2.50	0.92
New York:	66						56					
Min.....		0.77	0.44	0.23	1.85	0.65		0.78	0.48	0.23	1.86	0.60
Max.....		1.21	0.83	0.48	3.05	1.74		1.32	1.06	0.60	3.64	1.21
Aver.....		0.93	0.59	0.34	2.39	0.94		0.92	0.62	0.30	2.42	0.87
Ohio:	141						31					
Min.....		0.77	0.45	0.23	1.86	0.63		0.76	0.42	0.22	1.85	0.61
Max.....		1.61	1.04	1.01	4.41	1.82		1.23	1.04	0.45	4.24	1.16
Aver.....		1.07	0.68	0.39	2.99	1.12		0.95	0.64	0.31	2.74	0.92
Pennsylvania:	55						43					
Min.....		0.80	0.46	0.23	1.86	0.73		0.78	0.44	0.21	1.85	0.59
Max.....		1.36	1.08	0.63	4.28	1.29		1.26	1.00	0.60	4.49	1.31
Aver.....		1.01	0.68	0.33	2.73	1.01		0.97	0.64	0.33	2.84	0.93
Vermont:	50						63					
Min.....		0.77	0.35	0.23	1.86	0.58		0.77	0.37	0.24	1.86	0.51
Max.....		1.35	0.88	0.66	3.51	1.68		1.41	0.70	0.81	4.06	1.30
Aver.....		0.93	0.59	0.34	2.41	0.93		0.92	0.54	0.38	2.70	0.92
West Virginia:	3						7					
Min.....		1.10	0.74	0.29	3.61	1.22		1.09	0.65	0.44	3.04	1.13
Max.....		1.32	0.95	0.58	4.20	1.49		1.66	1.14	0.62	4.95	1.72
Aver.....		1.24	0.83	0.41	3.82	1.33		1.37	0.84	0.53	3.99	1.38
United States:	395						283					
Min.....		0.68	0.35	0.23	1.76	0.31		0.76	0.37	0.21	1.85†	0.51
Max.....		1.68	1.23	1.01	4.41	1.82		1.66	1.14	0.81	4.95†	1.72
Aver.....		1.02	0.64	0.38	2.72	1.04		0.95	0.62	0.33	2.68†	0.91
Canada:	86						80					
Min.....		0.77	0.36	0.23	1.85	0.21		0.76	0.31	0.24	1.86	0.62
Max.....		1.35	0.84	0.72	3.92	1.34		1.70	0.89	1.00	4.14	1.51
Aver.....		0.95	0.56	0.39	2.55	0.91		1.06	0.61	0.45	3.04	1.03

* J. Am. Chem. Soc. 1906, 28, 204.

† Cowles method: J. Am. Chem. Soc. 1908, 30, 1285.

‡ Determinations on 308 samples by Ross modification (U. S. Dept. Agr., Bur. Chem. 1910, Circ. 53): min. 2.20, max. 5.90, aver. 3.50.

SUMMARY OF ANALYSES OF PURE MAPLE SIRUP BY DIFFERENT ANALYSTS
(Results on dry basis)

	Ash				Alkalinity of ash			Lead No.		Malic acid No.	Conductivity No.
	Total	Sol.	In-sol.	Sol: insol.	Sol.	In-sol.	Sol.: insol.	Canadian	Winton		
	%	%	%	%							
Minimum:											
Bryan.....	0.68	0.35	0.23	0.53	41	41	0.21	1.76	0.29	...
Jones.....	0.77	0.45	0.25	0.7	46	55	0.45	0.65	...
McGill.....	0.69	0.33	0.12	1.37	1.05	0.30	...
Snell and Scott..	0.61	0.30	0.16	0.55	51	48	0.41	1.74	1.41*	0.38	112
Maximum:											
Bryan.....	1.68	1.23	1.01	3.86	122	208	1.83	4.41	1.60	...
Jones.....	1.32	0.72	0.78	2.6	102	145	1.67	1.11	...
McGill.....	1.38	0.79	0.75	6.56	2.38	1.16	...
Snell and Scott..	1.58	0.77	0.92	3.61	103	201	1.35	7.50	4.09*	1.46	230
Average:											
Bryan.....	1.00	0.63	0.37	1.84	75	97	0.81	2.70	0.84	...
Jones.....	0.92	0.58	0.34	1.78	79	83	0.98	0.82	...
McGill.....	0.89	0.56	0.33	2.83	1.75	0.77	...
Snell and Scott..	0.88	0.48	0.40	1.33	68	116	0.67	3.48	2.30*	0.75	147
Range:†											
Bryan.....	100	140	211	181	108	172	200	98	156	...
Jones.....	60	47	156	106	71	108	125	56	...
McGill.....	78	82	191	183	76	112	...
Snell and Scott..	110	98	190	230	76	132	140	166	117*	144	80

* Modified Winton lead No. † Percentage of average.

followed in order to secure comparable results. The precipitate in neither case is of the same composition in different samples.

Determination of the *electrical conductivity number*, as proposed by Snell,¹ is a valuable means of detecting the presence of common sugar. Snell and Scott's results² indicate that this value shows the narrowest range of all the values determined.

Conlin,³ by a rapid method devised by him, obtained the following average conductivity values: 400 samples of Canadian (Quebec) sirup 144; 500 samples of Maryland, Pennsylvania, New York, Vermont, and New Hampshire sirup 130; 250 samples of Maryland, Pennsylvania, and western New York sirup 135; 250 samples of Vermont, New Hampshire, and eastern New York sirup 124; 100 samples of Fancy and No. 1 southeastern Vermont sirup 130; 250 samples of Fancy Vermont and New York sirup 118; 250 samples of No. 3 Vermont and

¹ Trans. Roy. Soc. Canada 1913, Series 3, 7, 165; J. Ind. Eng. Chem. 1913, 5, 740.
² Loc. cit.
³ Ind. Eng. Chem., Anal. Ed. 1935, 7, 426.

New York sirup 137; and 150 samples of Mixed "Buddy" New York sirup 142.

CONSTITUENTS.—See also Introduction to Part I.

Acids.—The chief acid of maple sap and its products is *l-malic acid*. Bloor¹ showed that, when tissues of maple shoots are mixed with solutions of malic acid or malates and exposed to the light, there is an increase in reducing power and a decrease in acidity. Sando and Bartlett² state that malic acid exists in the sap both as normal and acid calcium malate.

Nelson,³ in maple sirup from two localities, isolated acids in the following amounts, calculated as grams per liter:

	Formic	Acetic	<i>l</i> -Malic	Citric	Fumaric	Succinic
Vermont	0.134	0.150	1.04	0.095	0.0056	not found
Michigan	0.121	0.085	0.81	0.110	0.0063	small amount

Findlay and Snell⁴ found *succinic acid* in maple sap.

In 16 per cent of the basic lead acetate precipitate overlooked by Fowler and Snell,⁵ Puddington and Snell⁶ identified malic and citric acids and traces of fumaric acid, but not succinic acid.

Maple Sugar Sand.—Hill, of the Vermont Agricultural Experiment Station, as early as 1888, showed that maple sugar sand is rich in *malic acid*. Warren⁷ showed that the deposit that separates during the concentration of the sap consists of crude calcium malate from which malic acid may be prepared. Von Lippmann⁸ isolated *d-tar-taric* and a small amount of *tricarballic acid* in addition to *l-malic acid*. Snell⁹ states that calcium malate constitutes approximately 70 per cent of the sand and that silica is also present; he¹⁰ suggests the use of this material for the economical manufacture of malic acid and

¹ J. Am. Chem. Soc. 1912, **34**, 534.

² J. Agr. Res. 1921, **22**, 221.

³ J. Am. Chem. Soc. 1928, **50**, 2006.

⁴ Canada J. Res. 1935, **13B**, 269.

⁵ Ind. Eng. Chem., Anal. Ed. 1929, **1**, 8.

⁶ Ibid. 1938, **10**, 132.

⁷ J. Am. Chem. Soc. 1911, **33**, 1205.

⁸ Ber. 1914, **47**, 3094.

⁹ Trans. Roy. Soc. Can. 1910, **13**, Sect. iii, 221.

¹⁰ Proc. 27th Ann. Meet. Vt. Maple Sugar Makers' Ass. 1920, p. 38.

its salts, stating that 50 to 160 tons of acid may be obtained annually from this source.

Analyses of 6 samples of washed maple sugar sand, made by Snell and Lochhead,¹ show the following range:

COMPOSITION OF WASHED MAPLE SUGAR SAND (SNELL AND LOCHHEAD)

	Water	CaO	MgO *	MnO†	P ₂ O ₅ †	SiO ₂	C ₄ H ₄ O ₄ ‡	CaC ₄ H ₄ O ₅
	%	%	%	%	%	%	%	%
Min. . . .	0.11	22.63	0.27	1.38	0.29	6.16	44.32	65.73
Max. . . .	0.69	25.74	0.88	1.87	0.99	18.55	53.73	79.67

* 4 samples. † 5 samples. ‡ Malic acid anhydride. || Calcium malate calculated from C₄H₆O₅

Nelson² found in maple sand *formic*, *acetic*, *l-malic*, *citric*, *fumaric acids* and traces of *d-tartaric* and *tricarballic acids*, also an unidentified acid the hydrazide of which melted at 173 to 175° C.

Carbohydrates.—As shown by the summary of analyses by Bryan and co-workers already given in tabular form, the dry matter of maple sirup and maple sugar consists essentially of crude *sucrose*, the other chief constituent being *invert sugar*.

Colors.—Standards for use in comparing maple sirups were prepared by Bryan from caramel made under fixed conditions; Balch,³ however, was unable to secure uniform colors by Bryan's method, even when every detail was carefully observed. The use of colored glass or solutions of inorganic salts is suggested.

Flavor.—Nelson⁴ brought out the presence of an *unstable phenolic substance* associated with a crystalline aldehyde melting at 74 to 76° C. similar in odor and properties to vanillin. He suggests the possible presence of other aldehydes. Risi and Labrie⁵ suggest that *hadromal*, the chief constituent of the aroma of boiling sap, is synthesized from the lignin of the wood. On sublimation, hadromal yields *vanillin*, *vanillic acid*, and *guaiacol*. *Coniferin*, present in small amount in the wood, is converted in September into resinous matter related to lignin. Findlay and Snell⁶ confirm Skazin's conclusion that the maple flavor is developed only after boiling.

¹ J. Ind. Eng. Chem. 1914, 6, 301.

² J. Am. Chem. Soc. 1928, 50, 2028.

³ Ind. Eng. Chem. 1930, 22, 255.

⁴ J. Am. Chem. Soc. 1928, 50, 2009.

⁵ Canada J. Res. 1935, 13B, 175.

⁶ Loc. cit.

Numerous attempts have been made to imitate the flavor of maple products, none of which has been successful; in fact, all the imitation flavors used in ice cream and cake frosting of which the writers have knowledge are decidedly unacceptable. In addition to extracts of hickory bark and fenugreek, constituents long used in imitation maple flavor, Nelson¹ mentions lovage, vanillin, and coumarin.

Robertson² takes advantage of the absence of *choline* in maple sap in the detection in maple products of fenugreek, which contains choline.

Various Constituents.—Findlay and Snell³ detected in maple sap an *unsaponifiable oil*, a *water-soluble substance* with the formula $C_{11}H_{21}O_9$ melting at $191.5^\circ C.$, and an *acetone-soluble substance* responding to color tests for lignin.

Enzymes.—Bois and Nadeau⁴ identified in maple sap two amylolytic enzymes: (1) *sucrogenetic amylase* and (2) *cellobiogenetic amylase*, both of which during the Winter hydrolyzed the starch of the roots without formation of maltose, but with formation of dextrans and ultimately the carbohydrates suggested by the names. The optima for the former are *pH* 6.6 and $8^\circ C.$, for the latter *pH* 4.8 and $50^\circ C.$, hence the formation of sucrose is greatest early in the Spring and of cellibiose later as the weather grows warmer. Findlay and Snell³ found a *glucosidase* in maple sap.

Bacteria.—Fabian and Buskirk⁵ isolated from maple sap a group of bacteria closely related to *Aërobacter aërogenes* producing ropiness in maple sirup.

Mineral Constituents.—In addition to determination of the solubility and alkalinity of the ash, determination of the ash constituents has been suggested as a means of distinguishing maple products from sirups prepared from brown sugar. The summarized results and ratios in the following table, based on figures obtained by Jones,⁶ Bryan,⁷ and Hortvet,⁸ bear on this point:

¹ J. Am. Chem. Soc. 1928, **50**, 2009.

² New York State Dept. Agr. Markets Rep. 1935, p. 55.

³ Loc. cit.

⁴ Naturaliste canadien 1935, 62, 106; Can. J. Res. 1938, **16B**, 114, 121.

⁵ Ind. Eng. Chem. 1935, **27**, 349.

⁶ Vermont Agr. Exp. Sta. Rep. 1904-5, **18**, 331.

⁷ Loc. cit.

⁸ J. Am. Chem. Soc. 1904, **25**, 1541.

COMPOSITION OF ASH OF MAPLE PRODUCTS

	Sam- ples	K ₂ O	CaO	P ₂ O ₅	SO ₃	$100 \times \frac{K_2O}{CaO}$	$100 \times \frac{SO_3}{CaO}$	$100 \times \frac{SO_3}{K_2O}$	$100 \times \frac{P_2O_5}{CaO}$
		%	%	%	%				
Maple Sirup									
Jones:	6								
Min.....		30.00	18.03	0.68	150	3.4	1.9	..
Max.....		38.98	23.98	2.30	181	12.7	7.2	..
Aver.....		34.76	20.74	1.55	168	7.8	4.6	..
Bryan:	100								
Min.....		24.55	13.20	1.08	0.00	77	0.0	0.0	4
Max.....		54.54	36.36	12.90	6.18	327	30	16	64
Aver.....		38.08	21.88	5.39	1.59	174	7	4	24
Maple sugar									
Jones:	4								
Min.....		18.26	21.03	1.51	57	5.2	5.1	.
Max.....		32.95	31.74	2.42	153	10.4	9.4	..
Aver.....		26.49	24.74	1.82	112	7.6	7.2	..
Brown sugar									
Jones*:	4								
Min.....		30.72	4.17	4.58	257	27	11	..
Max.....		55.40	21.62	17.78	949	157	58	..
Aver.....		41.58	13.19	8.29	435	83	25	..

* Including one by Hortvet.

Minor Mineral Constituents. *Manganese*.—Riou and Delorme¹ state that, although the manganese of cane sap is removed in the refining, maple sugar contains 0.01 to 0.12 mg. per kilo.

¹ Compt. rend. 1935, 200, 1132.

HONEY

To the casual observer, honey is the viscid saccharine substance stored in the comb by bees, but so simple a definition is regarded by food specialists as inadequate for two reasons: *first* it does not exclude the insipid product made by bees fed on sugar sirup, and *second* it does not distinguish between floral honey and that made wholly or in part by bees from saccharine exudations of plants whether gathered directly or indirectly from plant lice or other insects.

Standard Honey.—According to the *U. S. Standards* promulgated May 11, 1932:

1. Honey is the nectar and saccharine exudations of plants gathered, modified, and stored in the comb by honeybees (*Apis mellifica* and *A. dorsata*), is levorotatory, and contains not more than 25 per cent of water, not more than 0.25 per cent of ash, and not more than 8 per cent of sucrose.

2. Comb honey is honey contained in the cells of comb.

3. Extracted honey is honey which has been separated from the uncrushed comb by centrifugal force or gravity.

4. Strained honey is honey removed from the crushed comb by straining or other means.

Paragraph 1 of the *U. S. Standards* makes no provision for the exudation from insects gathered by bees and furthermore appears to exclude dextrorotatory honey, even though such may be made wholly from nectar and saccharine exudations of plants; it does, however, and very properly exclude the product of bees fed on sugar sirup, imitation honey made from commercial invert sugar, even though the chemical constituents are within the stated limits, and, of course, glucose and sugar sirups.

Formation of Floral Honey.—The nectar of flowers being thin and watery, concentration is essential in order to form honey. This evaporation of water takes place in the hive, exposure in thin films and air currents produced by the rapid motion of the wings of the bees being the chief factors. It is also claimed by some that alternate expulsion onto the tongue and sucking back into the honey sacs hastens the evaporation.

The saccharine matter of nectar consists to a large extent of sucrose which undergoes inversion before storage in the comb, hence the final product of normal floral honey is essentially *concentrated invert sugar sirup*.

Inversion of some of the sucrose appears to take place previous to the visit of the bee; at least, the presence of both *dextrose* and *levulose* has been demonstrated. Other constituents of nectar named by Küstenmacher¹ are *starch*, *gums*, *tannin*, *oxalic*, *malic*, and *tartaric acids*, and *inorganic matter*. The starch is converted into *dextrin*, the tannin oxidized, at least in part, and the inorganic salts partly assimilated by the bee during honey making.

Bonnier² states that the bee adds to the honey a drop of "venom" which probably acts as a preservative. He regards the constituents of the nectar as reserve material designed for utilization in the formation of the fruit and not merely as a lure for insects that effect cross fertilization. He further notes that the inversion of the sucrose takes place in a pocket of the esophagus by the action of invertase, also that the wax is produced in the body of the bee from honey and is secreted by glands located near the abdomen.

Sarin³ concludes from the results of feeding experiments with sucrose that dextrin is formed during inversion by what appeared to be a reversible action of invertase. Addition of citric or salicylic acid to sucrose fed to bees⁴ suppressed the biological processes concerned in the making and ripening of the honey.

Honeydew Honey.—Two kinds of honeydew are recognized, one exuded by the leaves of plants and utilized directly by the bee, the other produced by plant lice or leaf hoppers which feed on the exudations of plants. The leaves of various trees, less often non-woody plants, yield honeydew, but the amount that finds its way into European and American honey is not large. In Hawaii the insects feed on the sugar cane, and honeydew is one of the chief sources of honey.

Honeydew honey is inferior to floral varieties. As noted subsequently it is dextrorotatory and otherwise differs in composition from floral honey.

Noors Honey.—This name is applied to honey made from several species of *Euphorbia* which produces a burning sensation in the throat

¹ Biochem. Z. 1911, **30**, 237.

² Sugar 1919, **21**, 406.

³ Biochem. Z. 1921, **120**, 250.

⁴ Ibid. p. 259.

that persists for several hours. As examined by Juritz,¹ the honey is normal except that it shows a slight excess of non-sugar solids. The active principle was found to be present in the brown-colored oil obtained after removal of the wax from the ether extract; it is also present in the alcohol extract of *Euphorbia* flowers.

Feeding Sugar Sirup.—Reference has already been made under Standard Honey to feeding bees on sugar (sucrose) in the form of sirup, and further reference appears subsequently in connection with a consideration of sucrose under the head Constituents.

Fiehe² notes that honey made by bees fed on sugar sirup remains fluid on long keeping and has little tendency to crystallize. The color, aroma, mineral constituents, and diastase are deficient. The polarization is slightly to the left or to the right.

Fermentation of Honey.—Studies extending through eight years, carried out by Fabian and Quinet,³ brought out the presence of yeasts and molds in honey and the necessity of keeping within the critical moisture content of 21 per cent to prevent spoilage. Extracted honey at 20° C. absorbed 5 to 12 per cent of moisture on exposure to the air; comb honey stored in a dry place lost moisture, but when stored in a moist place it gained 3.5 to 5.7 per cent of moisture. Fermentation may be prevented by heating at 145° F. (63° C.) for 30 minutes.

Adulteration.—Toward the close of the last century strained honey was so often imitated that purchase in the comb was the only infallible assurance of purity. Three classes of saccharine sirup were used: (1) commercial glucose sirup or solutions of commercial grape sugar (dextrose), (2) cane sugar (sucrose) sirup, and (3) invert sugar sirup. The extent of foreign admixture was brought out by an extensive series of analyses carried out under the direction of Wiley⁴ by Huston, Nicholson, Rising, Scovell, Sharples, Stubbs, Wallace, Wiechmann, Weber, and McElroy.

Glucose Sirup.—The commercial sirup and other sirups, consisting essentially of dextrose and other products of acid hydrolysis, are detected by their high plus polarization, both direct and after inversion, the reading in the latter case being taken at ordinary temperatures and at 87° C.

¹ J. Dept. Agr. Union S. Africa 1925, 10, 334.

² Z. Unters. Lebensm. 1928, 55, 169.

³ Michigan Agr. Exp. Sta. 1928, Tech. Bul. 92.

⁴ U. S. Dept. Agr., Div. Chem. 1892, Bul. 13, Part VI.

Common Sugar Sirup.—Sirup made from common sugar has a plus polarization but less pronounced than that of sirups rich in glucose. After inversion the reading at 87° C. is approximately zero.

Invert Sugar Sirup.—Detection of invert sugar sirup presents greater difficulties than that of commercial glucose or sucrose since its saccharine constituents, in kind and amount, are much like those of real honey, as shown by analyses given under the head of Invert Sugar Sirup.

MICROSCOPIC STRUCTURE.—Aside from the observation of crystals of the constituent sugars which form during granulation, microscopic examination serves chiefly for the identification of pollen grains.

Pollen.—Bees derive muscular energy and warmth from honey, but their nitrogenous food is pollen which is separately collected. A sharp distinction should be drawn between pollen gathered for food which, although fed to the young in the special cells, is not intentionally stored in the comb, and pollen that is incidentally introduced into the honey in minute amount by bees that effect cross fertilization.

Since the pollen grains of different species differ greatly in size and form, much stress has been laid on the presence of pollen grains of one or more species as evidence of the source of honey or of the entire absence of any pollen grains as corroborating the results of chemical analysis that certain so-called honeys are factitious.

The writers wish to emphasize that evidence based on the determination of the kind and amount of pollen in honey should be treated with extreme caution, it being always remembered that pollen grains are an incidental constituent. Even when only one species furnishes the nectar, the amount introduced varies greatly with the conditions during storage, which cannot be accurately determined, also, in the case of strained honey, with the method of separation from the comb and of straining. When, as is common, several species contribute nectar, the complications are correspondingly greater. Since the amount of honey from a single species of plant cannot be estimated from the amount of pollen of that species present, a large amount of artificial honey mixed with a small amount of honey from a given species would escape detection. It is even possible to add pollen grains to an entirely factitious honey, thus deceiving the analyst, although the writers have never encountered such a sample.

Preparation of Sample.—The quantity of pollen present in honey is so small that it is desirable to accumulate the grains from a given amount in small compass, which is readily accomplished by dilution

and centrifuging. The sediment usually contains, in addition to the pollen grains, bits of insect tissues, yeast spores, hairs, and various other contaminations from the air. A small amount of this sediment may be added to a drop of pollen-free honey, concentrated sugar sirup, or dilute glycerin on a slide and examined directly. If, however, it is desired to determine the number, as well as the kind, of pollen grains in a weighed amount of the material, a cell such as designed for blood counts may be employed.

Histology.—Pollen is formed by the division of the pollen mother cell into four grains, usually rounded or elongated, which may cohere, though more often separate. Each grain consists of a single cell containing finely granular matter enclosed by a wall made up of two layers, an outer (*extine*) which is commonly the thicker and cuticularized and an inner (*intine*) which is largely composed of pectose. The extine may show fine lines perpendicular to the surface. The grains of some species have reticulations, spines, or various appendages, with or without oily or sticky secretions, on the surface, thus facilitating their attachment to the bee, thereby aiding cross fertilization and their introduction into the honey. Thin spots are often evident in the wall, each covered by a plug in the extine which the pollen tube pushes out as it develops. These spots are few in some species, numerous in others. In size the grains vary from less than 20μ to 200μ or over, one grain of squash pollen, for example, filling a circular field such as shown in the figures herewith.

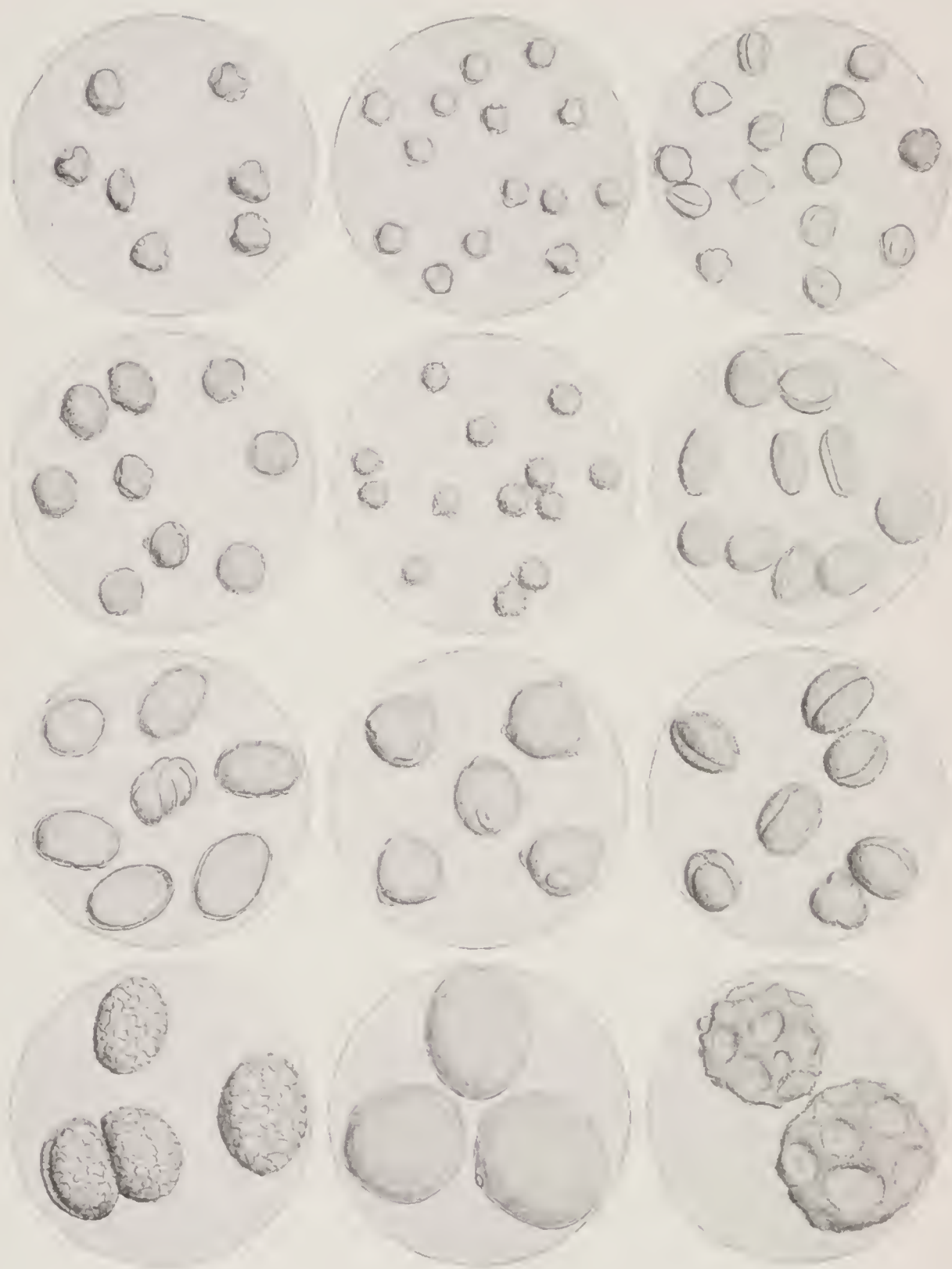
Young,¹ Niethammer,² and Griebel³ describe and illustrate pollens of various species occurring in honey. Figs. 1 to 12, showing pollen grains of twelve flowers from which honey is commonly made in the United States, are illustrative of types. In the identification of grains in honey, great care should be exercised, since those of many species are too much alike to warrant sweeping conclusions. Comparison with pollen of known origin, mounted in the same medium, is highly desirable.

PHYSICAL CHARACTERS. *Flavor.*—The epicurean value of honey depends on its delicate flavor, which is apart from its sweetness. The honey derived from each species has a more or less characteristic flavor which often is suggestive of the perfume of the flower. The flavor may be so pronounced as to permit positive identification

¹ U. S. Dept. Agr., Bur. Chem. 1908. Bul. 110, 70.

² Z. Unters. Lebensm. 1928, 55, 467.

³ Ibid. 1930, 59, 63, 441.



Pollen Grains. $\times 160$. (K.B.W.)

FIG. 1.—Linden

FIG. 2.—Red Clover

FIG. 3.—Sage

FIG. 4.—Lily

FIG. 5.—Clethra

FIG. 6.—Golden-rod

FIG. 7.—Honeysuckle

FIG. 8.—Maize

FIG. 9.—Blackberry

FIG. 10.—Sumac

FIG. 11.—Buckwheat

FIG. 12.—Cactus

by an expert. This, of course, is not possible if the honey is derived from several or numerous species.

Honeydew honey has a strong flavor which Browne¹ describes as resembling that of molasses.

Color.—Certain flowers, such as white and red clover yield a nearly colorless or light yellow honey; other species, such as buckwheat, a dark-colored honey. There appear to be exceptions to the rule, however, as samples examined by Browne, stated to be from the same flower, were in some cases light and in others dark.

Granulation.—Strained honey often becomes granular owing to the separation of dextrose (glucose) as crystals from the levulose (fructose) and other constituents which remain in solution as a thick sirup. The tendency to granulation is especially marked when the temperature is low.

Although without influence on the flavor and actually an advantage in spreading the honey on bread, granulation is commonly regarded as a defect. Browne states that packers of strained honey seek to avoid it by blending with honeys, such as sage and tupelo, and honeydew, that remain sirupy at all temperatures. Addition of glucose sirup is also a preventive of granulation, and this fact has often been made the excuse for grave frauds.

Fulmer, Park, and Williams² observed that granulation of honey did not take place when the water content was adjusted to less than 8.3 and over 20 per cent.

Polarization.—It is obvious from the figures given in the subsequent table that honey examined directly is usually levorotatory, owing to the strong predominance of invert sugar over sucrose, and that a dextrorotatory sample calls for explanation; furthermore that the levorotation of honey solution increases during standing for a day, as evidenced by the difference between the immediate and the constant polarization, a phenomenon, commonly observed in reducing sugars, known as bi- or multirotation.

Browne³ states that the granulation of honey, that is, the presence of crystals of glucose, causes an increase in multirotation and that any liquid honey displaying multirotation is probably especially susceptible to granulation. The solution is considered at first to contain high-polarizing molecular aggregates which gradually break down into simple low-polarizing molecules.

¹ U. S. Dept. Agr., Bur. Chem. 1908, Bul. 110.

² Iowa Agr. Exp. Sta., Ames, Rep. State Apiarist 1935, p. 62.

³ U. S. Dept. Agr., Bur. Chem. 1908, Bul. 110, p. 41.



Balavoine ¹ has shown that boiling for five minutes does not immediately destroy multirotation and that it may continue for three hours or longer after boiling and cooling. Ammonium hydroxide and sodium carbonate act more rapidly than boiling. Certain brown dextrorotatory honeys continue to show multirotation for many days.

CHEMICAL COMPOSITION.—The extensive analytical data reported by Wiley and collaborators, referred to above, were obtained for the most part on honeys sold on the market without guarantee of genuineness. The analyses by Browne ² and the study of the pollen grains by Young carried out later at the Bureau of Chemistry were on samples which were not only authenticated as to purity but also as to the predominating flower, although microscopic examination showed the presence of pollen grains of other species. A summary of the analytical results appears in the table on the following pages.

Browne, while warning against drawing sweeping conclusions, makes the following statement as to individual differences and peculiarities:

A comparison of the honeys by varieties shows usually a well-defined agreement in composition between the individual honeys of each particular class. The alfalfa honeys, for example, are usually marked by a lower content in dextrin and undetermined matter, and a higher sucrose content than any of the other varieties. In fact, two of the eight alfalfa honeys analyzed exceeded 8 per cent of sucrose, the limit set by the Standards Committee. The relatively high purity (low content in dextrans and undetermined matter) of the alfalfa honeys was shared, but to a less degree, by other members of the *Leguminosæ*.

The honeys of the *Compositæ* were about the average as regards organic non-sugars. The *Rosaceæ* were low in dextrin, but all high in undetermined matter. The buckwheats seemed characterized by an almost entire absence of sucrose and by the presence of tannin bodies. The basswood honeys were all relatively high in dextrin. This was also true of the sumacs, the poplar, oak, hickory, and other tree honeys, all these containing considerable quantities of honeydew. In addition to a high dextrin content, the latter were also characterized by a relatively high amount of ash. Honey gathered from plants or blossoms containing tannin, as the sumac and hop, usually gave pronounced reactions for tannin. The tupelo, mangrove and sage honeys were all distinguished by their high content of levulose.

¹ Mitt. Lebensm. Hyg. 1923, 14, 125.

² Loc. cit.

COMPOSITION OF AMERICAN AND HAWAIIAN HONEYS (BROWNE)

	Sam- ples	Water	In- vert sugar	Su- erose	Dex- trin	Acid as form- ic	Ash	Polarization				
								Direct			Invert	
								Imme- diate 20° C.	Con- stant 20° C.	87° C.	20° C.	87° C.
								° V.	° V.	° V.	° V.	° V.
American		%	%	%	%	%	%					
<i>Phanicææ</i>												
Cabbage palm.....	1	18.56	79.35	0.35	0.52	0.07	0.18	-18 0	-21.4	+ 3.6	-25.2	+ 2 5
Saw palmetto.....	1	19.22	73.63	0.69	2 14	0.10	0.32	-14 2	-16.8	+12.0	-20.0	+ 7.8
Palmetto-berry dew	1	18.34	73.51	1.92	3.05	0.25	0.69	-13 2	-17.2	+ 6.2	-21.2	+ 4.4
<i>Salicææ</i>												
Poplar.....	1	17.02	65.80	3.10	10.19	0.19	0.76	+ 6 7	+ 3.6	- 2.5	+20.9
Willow.....	1	19.11	71.47	0.95	2.75	0.07	0.35	-11.5	-12.9	+10.8	-15.6	+10.1
<i>Juglandææ</i>												
Hickory.....	1	16.05	65.89	2.76	12.95	0.12	0.78	+11 7	+ 7.8	+28.5	+ 3.4	+26.6
<i>Fagacææ</i>												
White oak.....	1	13.56	65.87	4.31	10.49	0.08	0.79	+20.9	+11.0	+32.3	+ 5.2	+28.6
<i>Moracææ</i>												
Hop vine.....	1	16.55	73.48	2.21	2 34	0.15	0.22	-10 9	-12.6	+10.8	-16.8	+ 9.7
<i>Polygonacææ</i>												
Buckwheat:	2											
Min.....		18.11	76.21	0.00	1.04	0.20	0.07	-14 7	-17.4	+ 8.0	-21.0	+ 5.8
Max.....		18.96	77.48	0.06	1.41	0.22	0.11	-14 5	-16.2	+ 8.4	-19.8	+ 6.1
Aver.....		18.54	76.85	0.03	1.22	0.21	0.09	-14 6	-16.8	+ 8.2	-20.4	+ 5.9
Heartsease.....	1	19.96	69.61	3.09	4.75	0.17	0.48	- 7.6	- 9.1	+12.2	-13.6	+11.0
Wild buckwheat....	2											
Min.....		17.92	73.98	0.00	0.34	0.10	0.08	-16.4	-18.9	+ 6.0	-22.4	+ 3.7
Max.....		17.96	78.89	0.60	1.91	0.14	0.12	-12.6	-18.0	+ 8.0	-20.9	+ 7.3
Aver.....		17.94	76.44	0.30	1.13	0.12	0.10	-14.5	-18.5	+ 7.0	-21.7	+ 5.5
<i>Magnoliææ</i>												
Whitewood.....	1	17.47	69.02	2.72	5.59	0.16	0.51	- 3.1	-4.9	+17.8	- 9.7	+15.4
<i>Rosacææ</i>												
Apple.....	2											
Min.....		14.55	73.11	2.72	0.37	0.05	0.04	- 4.3	- 8.9	+16.7	-13.8	+12.7
Max.....		16.78	73.22	4.66	0.40	0.05	0.13	- 1.2	- 8.2	+17.3	-13.7	+12.9
Aver.....		15.67	73.16	3.69	0.39	0.05	0.08	- 2.7	- 8.6	+17.0	-13.7	+12.8
Raspberry.....	1	16.26	76.52	1.88	0.80	0.06	0.05	-15.9	-19.4	+ 6.3	-23.8	+ 4.6
Wild red raspberry..	1	19.90	72.53	0.95	0.32	0.05	0.05	-15.5	-18.3	+ 7.0	-22.7	+ 5.5
<i>Leguminosææ</i>												
Alfalfa:	8											
Min.....		14.61	72.65	0.28	0.04	0.04	0.03	-17.5	-20.5	+ 4.6	-24.5	+ 3.5
Max.....		20.47	79.18	10.01	0.65	0.17	0.16	- 5.0	- 9.4	+15.3	-21.0	+ 7.7
Aver.....		16.56	76.90	4.42	0.34	0.08	0.07	-11.6	-15.1	+ 9.6	-23.0	+ 5.0
Alsike clover:	3											
Min.....		12.42	74.72	0.90	0.46	0.04	0.06	-10.6	-15.6	+10.4	-18.9	+ 9.1
Max.....		18.91	78.37	1.71	1.79	0.06	0.08	- 2.4	-12.8	+12.0	-16.2	+10.1
Aver.....		16.09	76.76	1.36	1.05	0.05	0.07	- 7.9	-14.0	+11.2	-17.7	+ 9.7
Sweet clover:	4											
Min.....		14.44	73.75	1.09	0.25	0.08	0.06	-16.0	-21.0	+ 3.7	-25.1	+ 2.4
Max.....		20.56	78.62	3.86	0.90	0.19	0.27	- 9.8	-14.5	+10.7	-20.8	+ 5.7
Aver.....		17.49	76.20	2.24	0.45	0.12	0.12	-12.1	-17.6	+ 6.8	-22.9	+ 4.7
White clover:	15											
Min.....		14.54	70.32	0.00	0.07	0.05	0.04	-16.8	-18.2	+ 7.4	-23.0	+ 5.1
Max.....		20.24	78.15	7.09	2.46	0.10	0.20	- 3.2	- 6.1	+16.4	-12.9	+13.8
Aver.....		17.64	74.92	1.77	0.82	0.06	0.07	- 9.7	-13.0	+11.7	-17.8	+ 9.3
Cat claw:	2											
Min.....		15.54	78.22	1.54	0.27	0.05	0.09	-15.0	-17.4	+ 7.9	-21.1	+ 5.7
Max.....		17.53	79.50	3.00	0.38	0.06	0.11	-14.8	-16.8	+ 8.2	-21.0	+ 7.0
Aver.....		16.53	78.86	2.27	0.33	0.06	0.10	-14.9	-17.1	+ 8.1	-21.1	+ 6.4
Loeust.....	1	15.38	75.34	1.24	2.13	0.06	0.08	-18.5	-21.4	+ 7.4	-26.1	+ 5.1

COMPOSITION OF AMERICAN AND HAWAIIAN HONEYS (BROWNE)—Continued

	Sam- ples	Water	In- vert sugar	Su- crose	Dex- trin	Acid as form- ic	Ash	Polarization				
								Direct			Invert	
								Imme- diate 20° C.	Con- stant 20° C.	87° C.	20° C.	87° C.
		%	%	%	%	%	%	° V.	° V.	° V.	° V.	° V.
Mesquit:	2											
Min.		15.39	79.90	1.12	0.25	0.06	0.08	-17.6	-20.5	+ 5.2	-23.8	+ 3.5
Max.		15.66	79.94	1.37	0.47	0.07	0.14	-17.0	-20.3	+ 5.4	-23.7	+ 4.0
Aver.		15.53	79.92	1.25	0.36	0.07	0.11	-17.3	-20.4	+ 5.3	-23.7	+ 3.7
Yellow wood	1	18.12	71.51	0.19	4.10	0.15	0.39	- 4.9	-7.0	+15.0	-10.6	+14.7
<i>Rutaceæ</i>												
Orange.	1	16.99	77.57	0.60	0.45	0.08	0.08	-11.7	-15.5	+ 8.8	-19.3	+ 6.6
<i>Anacardiaceæ</i>												
Sumac:	3											
Min.		18.17	68.61	0.36	1.66	0.09	0.21	-11.1	-13.8	+ 8.5	-17.6	+ 7.8
Max.		19.25	73.73	2.01	6.42	0.18	0.90	- 4.6	- 8.5	+14.6	-11.4	+14.4
Aver.		18.85	71.11	0.92	3.57	0.14	0.44	- 7.4	-10.5	+12.5	-14.0	+11.5
<i>Tiliaceæ</i>												
Basswood:	6											
Min.		15.66	69.85	0.00	1.50	0.05	0.11	- 9.3	-13.7	+ 9.7	-16.8	+ 8.6
Max.		20.25	78.55	2.03	7.58	0.18	0.35	+ 3.7	- 0.3	+23.7	- 1.3	+23.2
Aver.		17.42	75.14	0.72	3.07	0.10	0.20	- 5.2	- 8.9	+15.1	-12.3	+13.6
<i>Malvaceæ</i>												
Cotton:	3											
Min.		17.79	74.70	0.48	0.37	0.12	0.13	-16.5	-18.2	+ 6.6	-22.0	+ 5.1
Max.		18.91	80.69	1.64	1.83	0.20	0.28	- 2.3	- 5.0	+15.0	- 7.5	+13.8
Aver.		18.35	75.43	1.38	1.10	0.15	0.21	-14.5	-17.5	+ 6.8	-21.0	+ 6.1
<i>Myrtaceæ</i>												
Mangrove:	2											
Min.		18.83	75.94	1.14	0.29	0.07	0.16	-21.1	-24.8	+ 0.5	-27.9	- 0.7
Max.		19.53	77.04	2.33	0.82	0.08	0.24	-17.6	-20.8	+ 5.3	-24.4	+ 2.9
Aver.		19.18	76.49	1.73	0.56	0.08	0.20	-19.4	-22.8	+ 2.9	-26.2	+ 1.1
<i>Cornaceæ</i>												
Tupelo:	2											
Min.		16.29	72.09	1.65	1.47	0.05	0.07	-21.9	-24.6	+ 5.9	-29.3	+ 4.3
Max.		18.38	72.40	4.36	2.69	0.06	0.08	-20.6	-23.4	+ 6.2	-27.5	+ 4.6
Aver.		17.34	72.24	3.01	2.08	0.06	0.07	-21.3	-24.0	+ 6.1	-28.4	+ 4.5
<i>Ericaceæ</i>												
Laurel.	1	18.81	75.57	1.04	0.98	0.11	0.27	-16.1	-18.8	+ 5.3	-22.4	+ 4.6
White alder.	1	20.34	68.24	4.00	3.48	0.15	0.19	- 8.6	-11.1	+12.8	-14.5	+11.2
<i>Menthaceæ</i>												
Sage.	1	16.43	73.97	3.39	0.62	0.06	0.07	-18.1	-20.8	+ 5.8	-26.6	+ 3.1
Wild pennyroyal.	1	16.44	71.69	0.61	6.02	0.05	0.29	+20.4	+17.0	+35.8	+15.0	+35.0
<i>Cucurbitaceæ</i>												
Melon.	1	19.23	72.05	1.89	2.55	0.16	0.24	-11.4	-14.4	+ 9.3	-18.7	+ 8.6
<i>Compositæ</i>												
Arrow weed.	1	12.72	83.36	2.08	1.70	0.05	0.10	-14.0	-20.3	+ 6.9	-23.3	+ 4.6
Dandelion:	2											
Min.		14.53	76.21	1.57	0.45	0.05	0.11	-11.2	-12.8	+12.6	-20.1	+ 7.8
Max.		14.55	77.48	4.66	2.01	0.05	0.21	- 9.2	-12.0	+13.4	-17.7	+11.2
Aver.		14.54	76.84	3.12	1.23	0.05	0.16	-10.2	-12.4	+13.0	-18.9	+ 9.5
Golden-rod:	3											
Min.		16.20	67.81	1.06	1.56	0.06	0.09	-14.8	-16.4	+ 8.4	-21.1	+ 5.9
Max.		25.90	74.59	2.30	2.71	0.21	0.24	- 7.8	- 9.5	+13.0	-12.5	+11.3
Aver.		19.88	72.02	1.68	2.18	0.11	0.16	-10.7	-12.3	+10.9	-16.4	+ 9.4
Spanish needle.	1	19.18	69.58	1.23	3.45	0.06	0.05	-15.4	-18.6	+ 9.6	-20.5	+ 9.4
Wild aster.	1	19.43	76.00	0.64	1.42	0.15	0.25	-16.5	-21.4	+ 5.8	-22.4	+ 5.1
Mixed flowers:	5											
Min.		15.82	62.23	0.05	0.63	0.06	0.03	-13.8	-16.4	+ 8.7	-23.2	+ 6.1
Max.		26.88	76.85	2.66	3.66	0.11	0.35	+ 0.8	- 5.8	+16.8	- 9.8	+15.2
Aver.		19.46	72.59	1.44	2.31	0.09	0.18	- 7.0	-11.3	+12.9	-15.9	+10.7
Hawaiian												
<i>Leguminosæ:</i>												
Algarroba.	1	17.83	76.84	3.58	0.14	0.05	0.34	-17.8	-22.0	+ 2.7	-27.6	+ 1.0

COMPOSITION OF AMERICAN AND HAWAIIAN HONEYS (BROWNE)—Continued

	Sam- ples	Water	In- vert sugar	Su- crose	Dex- trin	Acid as form- ic	Ash	Polarization				
								Direct			Invert	
								Imme- diate 20° C.	Con- stant 20° C.	87° C.	20° C.	87° C.
		%	%	%	%	%	%	° V.	° V.	° V.	° V.	° V.
<i>Cactaceæ</i>												
Prickly pear.....	1	20.51	73.72	3.19	1.89	0.11	0.52	-11.9	-15.5	- 9.1	-17.9	+ 7.8
<i>Myrtaceæ</i>												
Blue gum.....	1	16.94	79.09	2.04	0.21	0.06	0.38	-18.8	-22.6	+ 2.3	-26.8	+ 0.4
Ohia lehua.....	1	20.00	75.57	1.03	0.46	0.15	0.21	-12.4	-15.9	+ 7.0	-18.7	+ 6.3
Mixed flowers:	2											
Min.....		17.82	70.33	1.56	0.29	0.08	0.32	-17.6	-20.0	+ 4.1	-26.1	+ 1.5
Max.....		20.59	77.62	2.81	3.60	0.15	0.79	- 4.8	- 8.2	+14.6	-10.3	+13.2
Aver.....		19.21	73.98	2.19	1.94	0.12	0.56	-11.2	-14.1	+ 9.4	-18.2	+ 7.3
Sugar cane honeydew..	1	15.46	64.84	5.27	10.01	0.15	1.29	+24.9	+17.8	+13.5	+34.8
Honeydew and mixed flowers:	4											
Min.....		15.88	66.85	0.36	1.77	0.07	0.48	-10.6	-15.1	-18.2	+ 7.8
Max.....		17.80	76.55	2.57	9.65	0.14	1.02	+ 9.8	+ 5.3	+ 1.9	+23.7
Aver.....		16.54	71.80	1.62	5.90	0.11	0.72	+ 0.4	- 4.4	- 7.1	+16.3
All Honeys												
Levorotatory:	92											
Min.....		12.42	62.23	0.00	0.04	0.04	0.03	-21.9	-24.8	+ 0.5	-29.3	- 0.7
Max.....		26.88	83.36	10.01	7.58	0.25	0.90	+ 3.7	- 0.3	+23.7	- 1.3	+23.2
Aver.....		17.70	74.98	1.90	1.51	0.08	0.18	-11.2	-14.7	+10.2	-19.2	+ 7.9
Dextrorotatory:	7											
Min.....		13.56	64.84	0.61	6.02	0.05	0.29	+ 6.7	+ 3.6	+28.5	- 2.5	+20.9
Max.....		17.80	71.69	5.28	12.95	0.19	1.29	+24.9	+17.8	+35.8	+15.0	+35.0
Aver.....		16.09	66.96	3.01	9.70	0.12	0.81	+14.8	+ 9.4	+32.2	+ 5.5	+27.6

The common names of plants given in the table and the corresponding Latin names are as follows:

American. Alder, white, *Clethra alnifolia* L.; alfalfa, *Medicago sativa* L.; apple, *Pyrus malus* L.; arrow weed, *Pluchea sericea* Nutt., Coville; aster, wild, *Aster* sp.; basswood, *Tilia*, sp.; buckwheat, *Fagopyrum fagopyrum* (L.) Karst.; buckwheat, wild, *Eriogonum* sp.; cat claw, *Acacia wrightii* Benth.; clover, alsike, *Trifolium hybridum* L.; clover, sweet, *Melilotus alba* Lam.; clover, white, *Trifolium repens* L.; cotton, *Gossypium herbaceum* L.; dandelion, *Taraxacum taraxacum* (L.) Karst.; golden-rod, *Solidago* sp.; heartsease, *Polygonum persicaria* L.; hickory, *Hicoria* sp.; hop, *Humulus lupulus* L.; laurel, *Kalmia latifolia* L.; locust, *Gleditsia triacanthos* L.; mangrove, *Rhizophora mangle* L.; melon, *Cucurbita* sp.; mesquite, *Prosopis* sp.; oak, white, *Quercus alba* L.; orange, *Citrus aurantium* L.; palm, cabbage, *Sabal palmetto* (Walt.) R. et S.; palmetto, saw, *Serenoa serrulata* (Michx.) Hook; pennyroyal, wild, *Mentha arvensis* L.; poplar, *Populus* sp.; raspberry, *Rubus* sp.; raspberry, wild, *Rubus* sp.; sage, *Salvia officinalis* L.; Spanish needle, *Bidens* sp.; sumac, *Rhus glabra* L.; tupelo *Nyssa aquatica* L.; whitewood, *Liriodendron tulipifera* L.; willow, *Salix* sp.; yellow wood, *Cladrastis lutea* (Michx.) Koeh.

Hawaiian. Algarroba, *Prosopis juliflora* (Swz.) D.C.; blue gum *Eucalyptus globulus* Labill.; Ohia lehua, *Metrosideros villosa* Smith; prickly pear, *Opuntia* sp.

The 49 samples of Hawaiian honey analyzed by Thompson¹ fall chiefly under the head of mixed honeydew and flowers. In the following table are given a summary of these analyses and of 4 samples of algarroba honey, also 1 analysis each of honey made from the flowers of Ohia lehua and honeydew:

¹ Hawaii Agr. Exp. Sta. 1908, Bul. 17, Part II.

COMPOSITION OF HAWAIIAN HONEY (THOMPSON)

	Samples	Water	Su- crose	Red. sugar	Ash	Polarization		
						Direct	Invert 30–34° C.	Invert 87° C.
		%	%	%	%	°V	°V	°V
Algarroba*:	4							
Minimum...	17.08	1.98	74.28	0.44	–19.7	–22.7
Maximum...	20.43	2.40	80.32	0.58	–17.7	–20.2
Ohia lehua †..	1	20.72	1.40	70.56	0.33	–11.6	–13.4
Honeydew ‡..	1	15.12	7.20	59.76	2.04	+24.5	+15.3	+36.0
Honeydew and flowers:	40							
Minimum...	15.31	1.6	55.92	0.59	–19.4	–17.3
Maximum...	18.94	6.3	77.28	2.10	+20.9	+15.4

* *Prosopis juliflora*. † *Metrosideros polymorpha*. ‡ Dextrin 0.339, acid 0.172%.

The average composition of Texas honey, according to Fraps,¹ is: water 18.51, protein 0.36, reducing sugars 75.71, sucrose 1.17, non-sugars 4.02, and ash 0.23 per cent.

The following table contains summaries of analyses of Cuban, Mexican, and Haitian honeys by Bryan,² French sanfoin honeys from Champagne by Ronnet,³ Dutch honeys by Voermann and Bakker⁴ and De Boer,⁵ Greek honeys by Emmanuel,⁶ and honeys from various countries (Argentina, Australia, Austria, Brazil, Chile, Cuba, Hungary, Italy, Jamaica, Mexico, Poland, Portugal, Russia, Spain, and the United States) by Fiehe and Stegmüller.⁷

One of the samples examined by Bryan gave a faint color with Browne's test, but the color was not sufficient to confuse the sample with honey containing an appreciable amount of commercial invert sugar. All Ronnet's samples gave negative tests. Fiehe's test gave faint reactions in 5 of Bryan's samples but none in Voermann and Bakker's or Fiehe and Stegmüller's samples, while Ley's ammoniacal

¹ Texas Agr. Exp. Sta. 1921, Bul. 272.

² Loc. cit.

³ Ann. fals. 1911, 4, 427.

⁴ Chem. Weekbl. 1911, 8, 784.

⁵ Ibid. 1933, 30, 401.

⁶ Ber. pharm. Ges. 1913, 23, 395.

⁷ Arb. kaisl. Gesundh. 1913, 44, 78.

silver test gave reactions with 18 out of 88 samples examined by the last-named investigator and was believed to be worthless.

COMPOSITION OF HONEYS FROM VARIOUS COUNTRIES

	Sam- ples	Water	In- vert sugar	Su- crose	Dex- trin	Acid as form- ic	Ash	Polarization				
								Direct			Invert	
								Imme- diate 20° C.	Con- stant 20° C.	87° C.	20° C.	87° C.
		%	%	%	%	%	%	° V.	° V.	° V.	° V.	° V.
Bryan												
Cuban:	33											
Min.....		16.05	68.09	0.00	0.29	0.00	0.07	-20.0	-21.1	+ 6.0	-23.4	+ 4.5
Max.....		27.00	77.56	2.99	3.96	0.43	0.39	- 6.1	- 8.6	+17.0	- 8.9	+15.4
Aver.....		21.07	71.77	0.94	1.43	0.14	0.22	-12.8	-14.1	+10.9	-15.8	+ 9.6
Mexican:	23											
Min.....		19.43	69.27	0.00	0.52	0.07	0.13	-22.9	-24.2	+ 3.2	-26.1	+ 2.9
Max.....		24.40	75.04	3.98	3.48	0.35	0.58	- 7.2	- 8.5	+15.7	- 9.3	+13.4
Aver.....		21.04	72.30	0.80	1.45	0.19	0.25	-12.4	-13.2	+11.3	-14.8	+10.2
Haitian:	16											
Min.....		18.60	69.15	0.00	0.26	0.03	0.06	-19.6	-20.7	+ 4.3	-22.7	+ 3.5
Max.....		25.05	76.73	2.44	1.65	0.28	0.45	-11.3	-12.5	+10.7	-13.3	+10.1
Aver.....		22.02	73.73	0.55	0.53	0.12	0.16	-15.8	-17.2	+ 7.7	-19.1	+ 6.6
Ronnet												
French:	19											
Min.....		15.75	76.95*	0.19	0.05	0.02	-2.20†	-2.32†
Max.....		19.80	82.41*	5.83	0.11	0.28	-1.22†	-1.40†
V. and B.												
Dutch:	42											
Min.....		17.70	70.00	0.05	0.10	- 4.0†
Max.....		23.70	5.00	0.15	0.55	- 1.5†
De Boer												
Dutch:	278											
Min.....		15.52	0.0	-11.5	-12.0
Max.....		33.06	7.6	+ 3.3	+ 1.3
Aver.....		20.27	1.8	- 6.3	- 7.1
Emmanuel												
Greek:	17											
Min.....		14.67	55.20	1.54	0.07	0.02
Max.....		31.68	78.24	4.81	0.15	0.44
F. and S.												
15 Countries:	111											
Min.....		14.94	61.96	0.12	0.03	0.03
Max.....		24.28	78.84	15.40	0.29	0.67
Aver.....		18.30	73.48	2.42	0.08	0.15

* Total sugars.

† 10% solution.

‡ Excepting 2 abnormal samples.

Fiehe¹ gives analyses of 17 samples of Cuban honey and lists the species of flowers which the bees visit. By a modification of the resorcinol method he obtained qualitative tests for commercial invert sugar in certain honeys produced near sugar factories.

¹ Z. Unters. Lebensm. 1928, 55, 460.

The following is the representative composition of Argentine honey based on 16 analyses by Ceriotti and Delpino:¹ water at 100 to 115° C. 15.42, reducing sugars 74.00, sucrose 0.72, total acid as formic 0.041, ash 0.093 per cent, and artificial sweetening agents none; polarimetric deviation of 20 per cent solution before inversion -4.72° , after inversion 5.00° ; volume of precipitate (albuminoids) according to Lund 0.7 cc.; reaction for artificial invert sugars according to Fiehe's resorcinol test negative.

Analyses of numerous samples of honey imported into Germany, including some from Hawaii, were made by Lendrich and Nottbohm.² The Hawaiian honey was low in acid (0.6 to 1.9, aver. **0.98** cc.), the others showing 0.6 to 3.5, aver. **1.88** cc. of normal alkali per 100 grams. Non-sugars were also low in the Hawaiian samples, the average being 1.26 per cent, whereas in other samples believed to be pure it was over 3 per cent.

An analysis by Perroncito and Issoglio³ of Italian honey from Friuli near Udine shows: specific gravity at 15° (diluted 1 : 2) 1.1212, water 17.30, protein 0.75, invert sugar 73.55, dextrose 36.40, levulose 37.15, sucrose 4.27, non-sugar 4.88, total acidity as formic 0.07, and ash 0.45 per cent; rotatory power $[\alpha]_D^{20}$ 2.8; Lund precipitate 1.8 cc.

Hungarian *Stachys* honeys, examined by Berkó and Kardos,⁴ contained 9.30 to 14.50 per cent of sucrose and the control samples 10.70 per cent.

Influence of Age.—As followed by DeBoer,⁵ the changes in the composition of unheated honey stored up to 22 years were chiefly a decrease in diastase, an increase in hydroxymethylfurfural causing a distinct Fiehe reaction, and an increase in ether-soluble matter titratable with iodine in alkaline solution. Sucrose, dextrose, levulose, and acids changed little or not at all with age.

CONSTITUENTS.—See also Introduction to Part I.

Proteins.—As compiled by König,⁶ early analyses by Erlenmeier and Reichenau show a protein content as high as 2.07 per cent. A single analysis by König himself gave 2.42 per cent, but those ob-

¹ Rev. facultad cienc. quím. (Univ. La Plata) 1930, **7**, 83; Chem. Abs. 1930, **24**, 5891.

² Z. Unters. Nahr. - Genusssm. 1911, **22**, 633; 1913, **26**, 1.

³ Ann. accad. agr. Torino 1919, **62**, 152.

⁴ Mezőgazdasági Kutatások 1937, **10**, 177.

⁵ Chem. Weekbl. 1934, **31**, 482.

⁶ Chem. mensch. Nahr.-Genusssm., Berlin, 1903, **1**, 915.

tained by Anthor and co-workers show a range of only 0.29 to 0.74 per cent. In 3 samples of honey, rich in honeydew, v. Raumer¹ reports 2.24 to 2.74 per cent of protein.

In Greek honeys, Emmanuel² found 0.037 to 0.582 per cent; in Italian honey Perroncito and Issoglio² found 0.75 per cent. Analyses by Browne² of American and Hawaiian honey from different flowers gave: alfalfa 0.106, algarroba 0.219, basswood 0.275, hickory 0.475, poplar 0.563, white oak 0.294, and whitewood 0.444 per cent of protein. Lund, as noted under Adulteration, regards a range of 0.34 to 0.43 per cent of protein as normal.

Langer³ uses a serological method for detecting artificial honey, the preparation injected into rabbits being a solution of the protein obtained by precipitation from dialyzed honey with ammonium sulphate. From the results of his experiments he concludes that this protein matter is formed in the body of the bee, not in the flower. This is the reverse of the view held by Küstenmacher.⁴

Moreau⁵ states that the presence of proteins may be demonstrated by the common reactions. He gives methods for the separation and determination of globulins and albumins and for the detection of proteoses and peptones. A summary of analyses of 10 samples follows: total proteins 0.394 to 1.50, proteins coagulable by heat 0.38 to 1.10, and total nitrogen 0.062 to 0.25 per cent.

Paine, Gertler, and Lothrop⁶ were able to remove the colloids of honey by ultrafiltration of a 25 per cent solution through collodion films. The honey before filtration contained 0.032 to 0.231, aver. **0.077** per cent of protein, and after filtration 0.009 to 0.085, aver. **0.042** per cent. The colloids removed contained 41.44 to 72.75, aver. **54.12** per cent of protein. Before filtration the average surface tension was about 22 per cent higher and the viscosity was slightly higher than after.

Tannin.—An astringent flavor in honey is due to tannin. Browne⁷ obtained more or less distinct tests for tannin in about half of the samples examined.

¹ Z. anal. Chem. 1894, **33**, 398.

² Loc. cit.

³ Arch. Hyg. 1909, **71**, 308; Biochem. Z. 1915, **69**, 141.

⁴ Loc. cit.

⁵ Ann. fals. 1911, **4**, 36.

⁶ Ind. Eng. Chem. 1934, **26**, 73.

⁷ Loc. cit.

Acids.—The acidity, calculated as formic acid, as given in analyses compiled by König, ranges from 0.03 to 0.21, average **0.11** per cent. These figures are in accord with results by Browne¹ which range from 0.04 to 0.25, average **0.09** per cent. Muttelet and Moroy² in 46 samples found 0.038 to 0.142 per cent. See also figures in foregoing analyses.

Although the acid commonly is considered to consist largely of *formic acid*, Farnsteiner³ found that only about 10 per cent was in that form, the remainder consisting largely of *malic acid*, although complete separation into the component acids was not attempted. Merl,⁴ in honey with a total acidity of 0.202 per cent, calculated as formic acid, showed that only 0.026 per cent, as determined by Wegner's method,⁵ was actually formic acid.

Heiduschka and Kaufmann⁶ have shown that only a small part of the acid of honey is volatile and not all of that is formic acid. Heiduschka⁷ reports as follows: total acids 12.0 to 20.2, volatile acids 1.7 to 1.9, *formic acid* (Wegner method)⁸ 0.41 to 1.2, *lactic acid* 2.3 to 2.8, *malic acid* 0.19 to 0.45, and *phosphoric acid* (P_2O_5) 0.025 to 0.032 per cent. The volatile acids other than formic were *butyric*, *valeric*, *caproic*, and *capric*.

Hydrogen-Ion Concentration.—According to Fiehe and Kordatzki,⁹ pure honey shows pH 3.8 to 4.3, average **3.9**, and artificial honey pH 3 to 4, average **3.2**.

Carbohydrates. *Invert Sugar.*—Although honey consists chiefly of invert sugar, dextrose and levulose are seldom present in equal amount. Browne¹⁰ states that in both floral and honeydew honeys levulose is always in excess, the average content in 92 samples being 40.50, whereas the average dextrose content was 34.02 per cent. These figures are in reasonably close agreement with the results of Soxhlet and Sieben,¹¹ who in 83 samples report an average of 38.65 per cent of levulose and 34.48 per cent of dextrose.

¹ Loc. cit.

² Ann. fals. 1923, **16**, 344.

³ Z. Unters. Nahr. - Genussm. 1908, **15**, 598.

⁴ Ibid. 1908, **16**, 385.

⁵ Z. anal. Chem. 1903, **42**, 727.

⁶ Z. Unters. Nahr. - Genussm. 1911, **21**, 375.

⁷ Pharm. Zentralhalle 1911, **52**, 1051; Schweiz. Wochschr. 1911, **49**, 725.

⁸ Z. anal. Chem. 1903, **42**, 727.

⁹ Z. Unters. Lebensm. 1928, **55**, 59.

¹⁰ Loc. cit.

¹¹ Z. Ver. Rübenzucker-Ind. 1884, p. 837.

Seventeen Greek honeys, analyzed by Emmanuel,¹ show the following range: levulose 23.14 to 40.28, dextrose 13.06 to 14.52 per cent. Results on other constituents appear in a foregoing table.

Auerbach and Bodländer² found that the ratio of levulose to dextrose, determined by a special method, varies from 106 : 100 to 119 : 100, and that the ratio increases during storage but is not changed by heating. Gronover and Wohnlick³ consider that the conclusions of Auerbach and Bodländer are not tenable. In only 8 out of 33 authentic samples was the levulose-dextrose ratio, as obtained by the Auerbach and Bodländer method, greater than 100 : 100. The range in invert sugar, as obtained by them, was 56.0 to 78.87 and of dextrose 26.3 to 41.0 per cent.

Sucrose.—The sucrose content in levorotatory honeys examined by Browne⁴ ranged from 0 to 10.01, the average being **1.90** per cent; in the dextrorotatory honeys it ranged from 0.61 to 5.28, the average being **3.01** per cent. Only 2 samples contained over 8 per cent of sucrose. Although the average sugar content was greater in the dextrorotatory samples, the chief cause of the plus polarization was the higher dextrin content. The maximum sucrose content in the analyses compiled by König is 12.91 per cent. Bakker⁵ employing Jolles' method,⁶ found in 16 samples of known purity less than 1 per cent.

Lippmann⁷ notes a sucrose content of 16.38 per cent in honey produced near a sugar factory, and even higher results have been obtained in unripened honey made by bees fed on sugar sirup. The amount of sucrose present in the finished honey is, however, only a fraction of that present either in the nectar or sugar sirup when gathered by the bees. In both cases the sucrose is gradually inverted, the difference being that in nectar the inversion process is well under way when gathered, whereas in sugar sirup no inversion takes place until the bee introduces the enzyme. Eventually, as noted by Browne,⁸ 80 per cent of the sucrose of the sugar sirup passes into invert sugar.

Honey traced to blueberries and mountain cranberry, examined by

¹ Loc. cit.

² Z. Unters. Nahr.-Genussm. 1924, **47**, 233.

³ Ibid. 1924, **48**, 405.

⁴ Loc. cit.

⁵ Rec. trav. chim. 1921, **40**, 600.

⁶ Z. Unters. Nahr.-Genussm. 1910, **20**, 631.

⁷ Z. angew. Chem. 1881, **1**, 633.

⁸ Loc. cit. p. 57.

Plahl and Fürstenau-Obadalek,¹ gave a blue color in the liquid heated for inversion.

Maltose.—Elser² isolated, from 4 samples of honey, maltose in the form of maltose-osazone and concluded that the sugar is a normal constituent of honey.

Melezitose, $C_{18}H_{32}O_{16} + 2H_2O$.—The manna formed upon Douglas fir trees is collected by bees during droughts. Since this manna is rich in the trisaccharide melezitose, Hudson and Sherwood³ suggest that the honey also contains this sugar. The same authors examined a honeydew honey from Pennsylvania that contained 20 per cent of melezitose which had crystallized in the cells. Honeydew honey from Maryland, where the bees collect a saccharine liquid containing melezitose deposited on the twigs of the Virginia pine by scale insects and aphids, also contained this sugar. The authors warn against condemning honey as being adulterated with sucrose when the increase in reducing sugar by acid hydrolysis is the only evidence. If the increase by invertase hydrolysis is much less than that by acid hydrolysis, the presence of melezitose is indicated.

Dextrin.—Browne's samples of levorotatory honeys contained 0.04 to 7.58, average **1.51** per cent of dextrin; the dextrorotatory honeys, 6.02 to 12.95, average **9.70** per cent. König's Compilation of 173 analyses shows an average of **2.89** per cent.

The dextrin of natural honey owes its origin, not to nectar, but chiefly or entirely to the exudations of plants, notably at the buds. In honeydew honey the exudations may to some extent pass through the body of plant lice or other insects.

Fiehe and Kordatzki⁴ demonstrated the presence in the dextrin of both natural and artificial honeys of 20 to 30 per cent of levulose molecules which were not removed by repeated recrystallization.

König and Hörmann⁵ studied the action of yeast of different strains on carbohydrates. Of special interest are the results on dextrin. Owing to its lower molecular weight, honey dextrin is more easily fermentable than malt dextrin or that prepared by acid hydrolysis. The yeast fermentation method of separation is more accurate than that by alcohol precipitation, but requires about 10 days.

¹ Z. Unters. Lebensm. 1937, **7**, 148.

² Mitt. Lebensm. Hyg. 1924, **25**, 92.

³ J. Am. Chem. Soc. 1920, **42**, 116.

⁴ Z. Unters. Lebensm. 1928, **55**, 602.

⁵ Z. Unters. Nahr.-Genussm. 1907, **13**, 113.

Pentosans.—Browne¹ secured the following results by the Kröber and Tollens' method on various honeys: algarroba 0.98, Hawaiian 1.00, basswood 0.83, hickory 1.01, poplar 0.99, and white oak 0.96 per cent.

Enzymes.—The chief enzyme of honey is *invertase*; *diastase* and *catalase* are also present in considerable amount. *Protease* appears to be present although the evidence with regard to this enzyme, as well as to *oxidase*, *peroxidase*, and *reductase*, is conflicting. *Inulase* is probably present; lactase and lipase appear to be absent.

Invertase.—Moreau² reviews the literature and furnishes proof, based on his own experiments, as to the presence of invertase, amylase, and catalase. Von Fellenberg³ concludes that invertase is present in greater amount than diastase since sucrose is hydrolyzed more rapidly than starch. The acidity appeared to be a much less important factor than age in influencing inversion. Gothe⁴ states that honey invertase is of both animal and vegetable origin. Contrary to Küstenmacher,⁵ who considers that it is derived from pollen, Caillas,⁶ and Sarin⁷ believe that it is produced by the bee.

Nelson and Cohn⁸ have demonstrated that increasing the percentage of sucrose above 4 per cent increases the rate of inversion by honey invertase, which is not the case with yeast diastase, furthermore that in the later stages the rate of honey invertase decreases more rapidly than that of yeast invertase and that the optimum pH for honey invertase is 5.5 to 6.3, depending on the stage of sucrose hydrolysis whereas the optimum pH for yeast invertase is 4.4 to 5.0 at all stages.

Nelson and Sottery⁹ observed that mutarotated dextrose (mixtures of α - and β -dextrose in equivalent proportions) and β -dextrose, also but to a lesser extent α -dextrose, in concentrations of 5 per cent or higher, retard the action of honey invertase on 10 per cent sugar solution, but in lower concentrations the mutarotated form and to a lesser degree the α -form accelerate the action, the optimum being 0.5

¹ Loc. cit.

² Ann. fals. 1911, 4, 65.

³ Mitt. Lebensm. Hyg. 1912, 2, 369.

⁴ Z. Unters. Nahr.-Genussm. 1914, 28, 273.

⁵ Loc. cit.

⁶ Compt. rend. 1920, 170, 589.

⁷ Biochem. Z. 1921, 120, 250.

⁸ J. Biol. Chem. 1924, 61, 193.

⁹ Ibid. 1924, 62, 139.

to 0.6 per cent. Mutarotated and β -levulose have less influence than the forms of dextrose. According to Papadakis,¹ pentoses, mutarotated xylose, *d*- and *l*-arabinose do not activate the hydrolysis of sucrose by honey invertase. The author also studied the influence of mercuric chloride and α -methylglucoside in conjunction with β -dextrose.

Amylase.—Among those who have established the presence of this enzyme and studied its action are Auzinger,² Moreau,³ Von Fellenberg,³ Gothe³ and Fiehe and Kordatzki.⁴ Gothe states that the amounts of amylase (diastase) and catalase are not proportional. Fiehe and Kordatzki have modified Gothe's method. Employing Koch's method they studied the diastatic action of honey amylase in solutions containing the same acid and salt content as honey.

Both Küstenmacher⁵ and Sarin⁵ agree that amylase owes its origin to the activities of the bee. On the other hand Fiehe,⁶ who gives diastase values of 1.0 and 2.5 for 2 samples of California honey and of 0.0 and 1.0 for 2 samples of French honey, all known to be pure, believe that the enzyme was derived chiefly from nectar and only in small part from the bee.

Bartels and Fauth⁷ suggest that the low diastase values of certain American honeys may be due to the high temperature of the region of production, as for example parts of California.

Catalase.—Auzinger,⁸ Moreau,⁸ and Gothe⁸ have established the presence of this enzyme in honey. Gillette⁹ confirms the presence of catalase and traces its origin to pollen and yeasts.

Protease.—By inoculating honey solution with wine yeast Lenz¹⁰ obtained an acid solution that rapidly digested egg white and herrings. Gothe,³ however, states that no protease is present in honey.

Oxidase, Peroxidase, and Reductase.—Auzinger¹¹ studied the reactions of these enzymes in honey. Moreau¹¹ was unable to find either anæro- or æro-oxidases.

¹ Ibid. 1929, 83, 561.

² Z. Unters. Nahr.-Genussm. 1910, 19, 65, 353.

³ Loc. cit.

⁴ Z. Unters. Lebensm. 1928, 55, 162.

⁵ Loc. cit.

⁶ Z. Unters. Lebensm. 1932, 63, 329.

⁷ Ibid. 1933, 66, 407.

⁸ Loc. cit.

⁹ J. Econ. Entomol. 1931, 24, 605.

¹⁰ Apoth. - Ztg. 1910, 25, 678.

¹¹ Loc. cit.

Flavor.—Illustrative of the dependence of the flavor on the species of flowers from which the bees collect the nectar is the presence of *methyl anthranilate* which Nelson¹ identified in the steam distillate from orange flower honey. This principle occurs also in other flowers and is characteristic of the grape.

Colors.—The color of honey is dependent to a large degree on the predominating species from which the nectar was derived. From a highly pigmented buckwheat honey Schuette and Bott² isolated *carotene* by a slight modification of Palmer and Eckles' method.³ Dumartheray⁴ has demonstrated that natural honey may contain coloring matter that dyes wool in an acid bath. Only when suspected samples give up to wool a color that shows definite reactions with acid or alkali is the presence of artificial color indicated.

Fluorescence in Ultra-Violet Light.—Orban and Stitz⁵ found that genuine honey shows a fluorescence which is more or less marked according to its origin. Heating up to boiling and cooling to room temperature did not change the fluorescence.

Mineral Constituents.—Browne⁶ found in levorotatory honeys 0.03 to 0.90, average **0.18** per cent of ash, and in dextrorotatory honeys 0.29 to 1.29, average **0.81** per cent. Utz⁷ reports that of 130 samples, apparently of known purity, 56 had less than 0.1 per cent, 46 between 0.1 and 0.2 per cent, 19 between 0.2 and 0.3 per cent, 4 between 0.3 and 0.4 per cent, and 5 over 0.4 per cent. Schwarz,⁸ however, out of 374 samples found only 18 with an ash content below 0.1 per cent and all but 2 of these appeared to contain artificial honey. Voermann and Bakker⁹ in 45 samples of pure honey, all but 8 produced in Holland, found 0.1 to 0.55 per cent of ash. The average ash content of coniferous honeys, as given in König's Compilation, is 0.60 per cent. See also figures in foregoing analyses.

Partial analyses of floral and honeydew honeys by Nottbohm¹⁰ show as follows:

¹ Ind. Eng. Chem. 1930, **22**, 448.

² J. Am. Chem. Soc. 1928, **50**, 1998.

³ J. Biol. Chem. 1914, **17**, 224.

⁴ Mitt. Lebensm. Hyg. 1923, **14**, 145.

⁵ Z. Unters. Lebensm. 1928, **56**, 467.

⁶ Loc. cit.

⁷ Z. angew. Chem. 1907, **20**, 2222.

⁸ Ibid. 1908, **21**, 436.

⁹ Z. öffentl. Chem. 1911, **17**, 461.

¹⁰ Arch. Bienenkunde **8**, 32; Chem. Abs. 1929, **23**, 4978.

COMPOSITION OF ASH OF FLORAL AND HONEYDEW HONEYS (NOTTBOHM)

	K ₂ O	Na ₂ O	CaO	MgO	P ₂ O ₅
	%	%	%	%	%
Floral:					
Minimum.....	30.50	5.54	2.12	1.50	1.65
Maximum.....	50.78	10.03	8.00	2.17	12.50
Honeydew:					
Minimum.....	52.59	3.16	0.52	0.71	6.64
Maximum.....	57.16	4.31	1.30	2.31	9.51

The result on all samples reported by Schuette and Hueninck ¹ range as follows: calcium 5 to 266, magnesium 7 to 126, phosphorus 23 to 58, and silica (SiO₂) 13 to 72 mg. per kilo. High mineral content (calcium excepted) was correlated with dark color. The percentage of ash and alkalinity of the ash for three types were: orange blossom 0.047 and 3.6, buckwheat 0.159 and 16.2 and "Titi" 0.263 and 34.5.

Determinations of *phosphoric acid* in the ash, by Kapeller and Gottfried,² show a range of 10 to 58 per cent, calculated as P₂O₅ in the ash. Emmanuel ³ reports 0.006 to 0.086, and Fiehe and Stegmüller ³ report 0.0075 to 0.0932, average **0.0198**, per cent of P₂O₅ in the honey.

Minor Mineral Constituents. *Iron.*—Honey 11.5 mg. per kilo, fresh basis (Peterson and Elvehjem).⁴

Manganese.—Honey, 25 samples, 0.04 to 4.4 mg. per 100 grams, calculated to the honey (Gottfried).⁵ Present in appreciable amount (Voermann and Bakker).⁶ Honey 0.36 mg. per kilo, dry basis (Peterson and Skinner).⁷

Copper.—Honey 2.0 mg. per kilo, fresh basis (Lindow, Elvehjem, and Peterson).⁸

¹ Food Res. 1937, **2**, 529.

² Ber. Nahrmtl. Unters. Amt. Magdeburg 1913, **15**, 16.

³ Loc. cit.

⁴ J. Biol. Chem. 1928, **78**, 215.

⁵ Pharm. Zentr. **52**, 787.

⁶ Loc. cit.

⁷ J. Nutrition 1931, **4**, 419.

⁸ J. Biol. Chem. 1929, **82**, 465.

INVERT SUGAR SIRUP

SIRUPS, consisting chiefly of invert sugar prepared by treatment of sugar of various grades, molasses, refined sirups, and various waste products with invertase, acids, salts, or other chemicals are now used to a considerable extent in brewing, in the manufacture of artificial honey, and in other food industries.

Jordan and Chesley¹ state that during the year 1916 over 2,000,000 gallons of commercial invert sugar sirup representing a value of over \$1,000,000 were used in several industries. They separate the sirup into light and dark and each of these into four classes according to the composition and probable source. Of the light sirups classes A and C showed good inversion, but the former appeared to contain mineral matter resulting from neutralization of the acid or added for some special purpose and the latter was low in total sugars owing to the inversion of 75 per cent sucrose solution. Class B did not show good inversion, and class M was of miscellaneous products. Of the dark sirups classes A' and B' were similar and were probably made from mixtures of light sirup and molasses or low-grade sugar which in B' contained less than 90 per cent of sucrose; class C' was made from raw sugar with at least 98 per cent of sucrose or 50 per cent of sirup and 50 per cent of bright molasses; and class M' was of miscellaneous samples. The range of invert sugar, sucrose, and ash in the samples in each class follows:

COMPOSITION OF INVERT SUGAR SIRUP (JORDAN AND CHESLEY)

	Invert sugar	Sucrose	Ash
	%	%	%
Light sirup:			
Class A	76.70-78.60	0.98- 3.33	0.01-0.12
" B	68.08-76.80	2.56-11.88	trace -0.11
" C	73.69-75.82	0.49- 3.47	trace
" M	44.05-75.85	2.44-33.57	trace -0.40
Dark sirup:			
Class A'	36.92-51.32	15.49-35.09	0.39-2.44
" B'	29.23-53.28	23.77-46.63	0.22-1.03
" C'	35.19-73.65	4.01-35.84	0.05-3.51
" M'	18.00-68.67	6.35-52.51	0.04-2.41

¹ J. Ind. Eng. Chem. 1917, 9, 756.

ARTIFICIAL HONEY.—Carefully prepared invert sugar sirup, suitably flavored, closely resembles true honey in composition (See Adulteration under Honey). Although its sale as honey and its admixture with the genuine product without suitable labeling are obviously frauds, the product has a legitimate use in feeding bees during a shortage of honey or as a honey substitute. During the World War, when there was a shortage of honey in Germany, formulas for its preparation were officially supplied to consumers.

Herzfeld¹ heated 1 kilo of refined sugar, 300 cc. of water, and 1.1 grams of tartaric acid at 110° C. until the liquid became a golden yellow. An addition to this sirup of rank-flavored heather or linden honey resulted in a palatable product. Sauer² advocated the use of lactic acid; Paul,³ of lemon juice or citric acid; and Willaman,⁴ who had specially in mind the Winter feeding of bees, of invertase.

Beythien⁵ recommends legal regulation of the raw material used and the labeling. He examined honey-powders consisting of sucrose, citric or tartaric acid, color, and flavor, also "honey-aroma" consisting of citric, tartaric, or formic acid mixed with potato meal, gelatin, or other inert matter, suitably colored and flavored.

Behre and Ehrecke⁶ give precautions to be observed in the manufacture of artificial honey and suggest the compulsory addition of starch or phenolphthalein to serve as an indicator in case of suspected misuse. Their analyses of 58 samples show 18–20 per cent of water, less than 20 per cent of unchanged sucrose (excepting a few cases with over 25 per cent), and acidity equivalent to 0.2–4.6 cc. of normal acid per 100 grams.

The composition of artificial honey made by the Herzfeld process and reported by Browne⁷ and the average of 10 analyses given by Borries⁸ follow:

COMPOSITION OF ARTIFICIAL HONEY

	Water	Invert sugar	Sucrose	Dextrin	Non-sugar solids	Undetermined
	%	%	%	%	%	%
Browne	16.32	73.38	4.36	1.08	4.86*
Borries	18.00	73.8	4.5	3.6	0.10

* Acid as formic 0.06%; ash none.

¹ Deut. Zuckerind. 1906, **31**, 1988.

² Pharm. Ztg. 1915, **60**, 798.

³ Sueddeutsch. Apoth.-Ztg. 1916, **56**, 272; Münch. med. Wochschr. 1916, **63**, 858.

⁴ Sugar 1926, **28**, 409. ⁵ Z. Unters. Nahr.-Genussm. 1919, **38**, 159; 1921, **41**, 300.

⁶ Chem. Ztg. 1919, **43**, 153.

⁷ Loc. cit. p. 67.

⁸ Arb. Reichsgesundh. 1920, **52**, 650.

Browne's sample polarized as follows: direct at 20° C. -6.2° , constant at 20° C. -9.5° , invert at 20° C. -16.94° , invert at 87° C. $+4.84^{\circ}$.

Tests for Invert Sugar Sirup.—Certain qualitative colorimetric tests, rather than quantitative methods, are the chief dependence. The following are the most important: Ley's ammoniacal silver test,¹ which is essentially a general test for aldehydes, Browne's aniline acetate test,² and Fiehe's resorcinol-hydrochloric acid test,³ the two last tests depending on the presence of furfural and its derivatives, notably β -hydroxy- δ -methyl furfural.

Ley's test was found by Browne⁴ and Voermann⁵ to be unreliable in certain cases and is not recommended by Bryan; Witte⁶ and some others, however, have found it useful.

Browne's test has been successfully employed by Bryan⁷ and other American chemists. The *Feder test*⁸ may be regarded as a modification, since the essential difference is the use of aniline hydrochloride instead of the acetate. Greenleaf and Browne⁹ state that although Browne's test is not so sensitive as Fiehe's, the results are more easily interpreted.

Fiehe's test has been shown by v. Raumer,¹⁰ Drawe,¹¹ Klassert,¹² and Bremer and Sponnagel¹³ to give positive reactions when applied to genuine honey that has been heated one-half to two hours on a boiling water-bath, hence it is claimed to be merely a test of whether or not the product has been heated. V. Raumer's statement that the reacting substance is neither furfural nor an aldehyde lacks confirmation. Luehrig¹⁴ obtained the test on unheated honey made by bees from a mixture of sucrose and glucose. Hertkorn¹⁵ and Bremer and Sponnagel¹³ are particularly severe in their criticisms of this test, the latter

¹ Pharm. Ztg. 1902, **47**, 603; Z. angew. Chem. 1907, **20**, 993.

² Loc. cit. p. 68.

³ Z. Unters Nahr.-Genussm. 1908, **16**, 75.

⁴ Loc. cit.

⁵ Z. öffentl. Chem. 1910, **16**, 401.

⁶ Z. Unters. Nahr.-Genussm. 1909, **18**, 625.

⁷ U. S. Dept. Agr., Bur. Chem. 1912, Bul. **154**.

⁸ Z. Unters. Nahr.-Genussm. 1911, **22**, 412.

⁹ J. Ass. Off. Agr. Chem. 1929, **12**, 319.

¹⁰ Z. Unters. Nahr.-Genussm. 1908, **16**, 517; 1909, **17**, 115.

¹¹ Z. öffentl. Chem. 1908, **14**, 352.

¹² Z. Unters. Nahr.-Genussm. 1909, **17**, 126.

¹³ Ibid. 1909, **17**, 664.

¹⁴ Pharm. Zentr. 1909, **50**, 605.

¹⁵ Chem. Ztg. 1909, **33**, 481.

because genuine honey, unheated as well as heated, often gives the reaction, while adulterated honey in some cases does not.

On the other hand, Utz¹ did not secure a reaction with heated honey by Fiehe's test but did by Ley's test. Invert sugar sirup made with organic acids gave negative reactions. Riechen and Fiehe,² although noting that a slight rose color sometimes appears after heating on a boiling water-bath one hour, claim that this color would not be confounded with that formed in imitation honey. Ledent³ found the test reliable, as did also Witte⁴ and Muttelet.⁵ Jägerschmid⁶ obtained no reaction in honey heated thirty minutes; he considers that the substances causing the color reaction are furfural and its methyl and hydroxymethyl derivatives. Bryan,⁷ Hartmann,⁸ Halphen,⁹ Nelson,¹⁰ and Weiss¹¹ have modified the test so as to obviate the interference of traces of certain volatile oils and other minor constituents or otherwise to render the test more efficient. Troje's modification,¹² treating directly with an ether solution of resorcinol, has been shown by Fiehe¹³ to be inaccurate.

Weiss,¹¹ employing ethyl acetate instead of ether for extraction of the reacting principle, found 0.0322 to 0.2255 per cent of *β*-hydroxy-*δ*-methyl furfural in artificial honeys but none in genuine. Lampitt, Hughes, and Rooke,¹⁴ who use ether for extracting the furfural and its hydroxy methyl derivative, found that storage of heated honey for one year did not cause a formation of furfural or derivatives.

Jägerschmid's acetone-hydrochloric acid method,¹⁵ although endorsed by Ledent,¹⁵ does not appear to have met with general favor.

Lund's Protein Test is recommended by several authors. Lund¹⁶

¹ Z. angew. Chem. 1908, **21**, 2315.

² Chem. Ztg. 1908, **32**, 1090.

³ Bul. soc. chim. belg. 1914, 73.

⁴ Loc. cit.

⁵ Ann. fals. 1911, **3**, 503.

⁶ Z. Unters. Nahr.-Genussm. 1909, **17**, 113.

⁷ U. S. Dept. Agr., Bur. Chem. 1912, Bul. **154**, 15.

⁸ Z. Unters. Nahr.-Genussm. 1911, **21**, 374.

⁹ Ann. fals. 1912, **5**, 106.

¹⁰ J. Ass. Off. Agr. Chem. 1929, **12**, 323.

¹¹ Z. Unters. Lebensm. 1929, **58**, 320.

¹² Z. Ver. deut. Zucker-Ind. 1925, **75**, 635.

¹³ Z. Unters. Lebensm. 1928, **56**, 200.

¹⁴ Analyst. 1929, **54**, 381, 736.

¹⁵ Loc. cit.

¹⁶ Z. Unters. Nahr.-Genussm. 1909, **17**, 128; Mitt. Lebensm. Hyg. Schweiz.-Gesund. 1910, **1**, 38.

notes that the determination of nitrogen, or better pure protein (albuminoid) nitrogen, distinguishes genuine from imitation honey; in the former he found 0.34 to 0.43 per cent of nitrogen, in the latter 0.06 to 16 per cent. Marked distinctions were also obtained by measuring the bulk of the protein precipitate formed with 5 per cent tannin solution or phosphotungstic acid-sulphuric acid solution. With the tannin reagent, the range for genuine honey was 1.60 to 2.30 cc. and for imitation honey 0 to 0.30 cc.; with the phosphotungstic acid-sulphuric acid reagent, the range for genuine honey was 0.60 to 2.70 and for imitation honey 0 to 0.50 cc.

Ash Test.—Several authors advocate the determination of total ash and phosphoric acid in the ash as means for distinguishing natural from imitation honey. Figures obtained on genuine honey are given in a subsequent section.

Precipitin Test.—Reigler¹ prepared an antiserum which caused precipitation in genuine honey; Langer² perfected the method and showed that the antigens come from the bee and not the plant. This being so, it is doubtful that the test serves to detect the product resulting from feeding bees sugar sirup. Galli-Valerio and Borñañd³ employed the method successfully. Thöni⁴ confirms Langer's findings and gives results in terms of the volume of the precipitate. Heating, if kept well within the boiling point, does not appear to interfere seriously. Thöni gives full instructions for conducting the test and points out its advantage as compared with chemical and physical methods.

¹ Oesterr. Chem.-Ztg. 1902, p. 97.

² Arch. Hyg. 1909, 71, 308; Biochem. Z. 1915, 69, 141.

³ Z. Immunitäts. 1911, 7, 371.

⁴ Mitt. Lebens. Hyg. 1911, 2, 80; 1912, 3, 74.

STARCH SUGAR AND GLUCOSE

THE nature of the commercial products made by the complete or partial hydrolysis of starch is indicated by the following definitions given in the *U. S. Standards*:

1. Starch sugar is the solid product made by hydrolyzing starch or a starch-containing substance until the greater part of the starch is converted into dextrose. Starch sugar appears in commerce in two forms, anhydrous starch sugar and hydrous starch sugar. The former, crystallized without water of crystallization, contains not less than ninety-five per cent (95%) of dextrose and not more than eight-tenths per cent (0.8%) of ash. The latter, crystallized with water of crystallization, is of two varieties: 70 sugar, also known as brewers' sugar, contains not less than seventy per cent (70%) of dextrose and not more than eight-tenths (0.8%) of ash; 80 sugar, climax or acme sugar, contains not less than eighty per cent (80%) of dextrose and not more than one and one-half per cent (1.5%) of ash.

The ash of all these products consists almost entirely of chlorids and sulphates.

2. Glucose, mixing glucose, confectioner's glucose, is a thick sirupy, colorless product made by incompletely hydrolyzing starch, or a starch-containing substance, and decolorizing and evaporating the product. It varies in density from forty-one (41) to forty-five (45) degrees Baumé at a temperature of 100° F. (37.7° C.), and conforms in density, within these limits, to the degree Baumé it is claimed to show, and for a density of forty-one (41) degrees Baumé contains not more than twenty-one per cent (21%) and for a density of forty-five (45) degrees not more than fourteen per cent (14%) of water. It contains on a basis of forty-one (41) degrees Baumé not more than one per cent (1%) of ash, consisting chiefly of chlorids and sulphates.

Glucose, as defined above, is made in the United States from maize and is known by some manufacturers as Corn Sirup.

Much confusion and controversy has resulted from the application of the English term glucose to both the sugar *d*-glucose or dextrose and the sirup, made by the hydrolysis of starch, containing in addition to *d*-glucose both maltose and dextrin. The German term "Stärke-sirup" (starch sirup) is free from this ambiguous meaning. In this work the term dextrose (*d*-glucose) is used for the pure monosaccharide and the term glucose sirup for the sirupy commercial product.

Process of Manufacture.—The hydrolysis of the starch is effected by heating with dilute sulphuric or hydrochloric acid under pressure, the time of heating and pressure being greater for complete conversion into dextrose than for partial conversion when glucose sirup is the end product. After boiling, the acid is neutralized with calcium or sodium carbonate, the latter being preferable when hydrochloric acid is the hydrolytic agent, as is now customary, since the mineral

residue consists of a small amount of common salt. Clarification is effected by bone black, after which treatment the solution is evaporated in vacuum pans to a thick sirup or, in the case of dextroses, the crystallization point or the solid condition according to the product desired. The higher grades of dextrose, after crystallization, are freed from the mother liquor by hydraulic pressure or centrifuging. Washing with water while in the centrifuge effects a further purification.

After partial hydrolysis, as carried out in the manufacture of commercial glucose sirup, dextrin and maltose, as well as dextrose, are present in the liquid, whereas in complete hydrolysis all the starch is converted into dextrose.

Uses.—Enormous quantities of dextrose and glucose sirup are used in the United States in the manufacture of confectionery, in the brewing industry, in the sweetening of fruit products, as the chief ingredient of certain table sirups, etc. Several sirups, sold under trade names in retail containers, consist of mixtures of glucose sirup (corn sirup) and refiners' sirup. There has been much controversy over the labeling of these mixtures in compliance with food laws.

CHEMICAL COMPOSITION. Commercial Glucose.—Bryant,¹ in a study of the changes taking place during hydrolysis, found that the determination of reducing sugars in terms of dextrose gives a fairly close measure of the total fermentable sugars present, furthermore that the maltose, the chief fermentable constituent, is much more constant in amount than the dextrose. The lower the amount of reducing sugars, the lower the dextrose, no dextrose at all being present in the early stages. These facts, as well as the general composition of European and American glucose sirups, are brought out in the following table:

COMPOSITION OF DRY SUBSTANCE OF COMMERCIAL GLUCOSE (BRYANT)

	Samples	Dextrose	Maltose	Dextrins	Ash
		%	%	%	%
Corn glucose (American) . . .	12				
Minimum	12.1	24.2	47.0	0.3
Maximum	21.6	36.6	59.5	0.7
Potato glucose (European) ..	1	19.8	35.0	44.8	0.4
Glucose 1/3 conversion	0.0	30.8	68.8	0.4
" 2/3 "	8.6	27.1	63.9	0.4
" full "	18.1	27.4	54.1	0.4

¹ 8th Int. Cong. App. Chem 1912, 13, 47.

Twenty years later Bryant and Jones¹ stated that the reducing sugars of common corn sirup in ordinary work may be considered to consist of one-third dextrose and two-thirds maltose and that the undetermined carbohydrates may be classed as dextrans. In glucose of higher conversions, the ratio of dextrose to maltose is nearer 1 : 1.

Although some believe that maltose, as formed by acid hydrolysis, is immediately changed to dextrose, the weight of evidence is in favor of the view that it exists as one of the constituents of commercial glucose sirup.

Dextrin, $(C_6H_{10}O_5)_n$.—This generic term applies to a number of polysaccharides intermediate between starch and maltose. The four dextrans, long regarded as being links in the chain, are *amylodextrin*, *erythrodextrin*, *achroodextrin*, and *maltodextrin*. Only the first two give color reactions with iodine solution, the color with amylodextrin being blue and with erythrodextrin being red.

Commercial dextrin is commonly prepared by roasting dry starch with very dilute nitric acid. It has practically no reducing power. Its specific rotation is about +195.

Maize vs. Potato Glucoses.—Behre, Düring, and Ehrecke² were unable to detect any marked difference in the sugars of the solid products and sirups from corn and potato starch. Parow³ also found practically no difference by chemical methods but notes that potato glucose usually was less prone to show a color when heated to 145° C. Such coloration is stated to be due to fat and proteins, the former being added to prevent frothing in the vacuum pan. When only 0.06 per cent of fat and 0.09 per cent of protein were present, the coloration was slight, but when two to three times these amounts were present, the discoloration was strongly marked.

¹ Ind. Eng. Chem. 1933, **25**, 98.

² Z. Unters. Nahr.-Genussm. 1921, **42**, 242.

³ Z. Spiritusind. 1922, **25**, 229.

VARIOUS PRODUCTS

Malt Sirup.—During the years of sugar shortage after the World War the manufacture of malt sirup from barley, corn, potatoes, and other starchy products was recommended by the experts of the United States Department of Agriculture.¹ The equipment of an ordinary brewery, with the addition of evaporating apparatus, suffices for its production. Dale² states that degerminated maize meal, maize starch, and other starchy maize products may be used as raw materials, the hydrolyzation being effected by barley malt. He confirms the claims of government experts that the sirup has a pleasant flavor. The sweetness is intermediate between glucose and sugar sirups of the same concentration. Since it does not crystallize, it is adapted for blending with honey and various sirups which are prone to solidify. The average composition follows: water 20, protein 0.5, maltose 64, dextrin 15, and ash 0.5 per cent.

Carob Bean Sugar and Molasses.—The structure and composition of the carob bean are treated in Volume II.

The pod of this bean (*Ceratonia Siliqua* L.), according to Oddo,³ contains 20 to 34 per cent of sucrose and 10 to 20 per cent of reducing sugar. Oddo and DeFonzo⁴ employ alcohol and other organic solvents for its extraction. The sugar of the first crystallization is yellow and has a pleasant odor; after recrystallization it is colorless and odorless. The molasses is suited for use in confectionery.

Grape-vine Sirup.—Carrière,⁵ by the acid hydrolysis of the carbohydrates in grape-vine prunings, obtained a solution containing 8 per cent of sugars. The liquid may be fermented or concentrated to a sirup.

¹ Weekly News Letter 1919, 7, No. 15.

² Sugar 1920, 22, 331.

³ L'ind. sacc. ital. 1928, 21, 460.

⁴ Giorn. chim. ind. appl. 1927, 9, 400.

⁵ Rev. vit. 1929, 70, 37; 71, 58.

CARAMEL

THE mixture of decomposition products formed by heating sucrose, glucose, molasses, or other saccharine products to 190 to 220° C. is known as caramel or burnt sugar. When molasses or other substance of indefinite composition containing inorganic as well as organic impurities is used as the raw material, the resulting caramel is of particularly variable composition, however carefully the process may be conducted. A product of reasonably definite composition is obtained by heating ash-free white sugar of the highest commercial grade for a fixed time at a fixed temperature, but the chemical nature, color, and other properties of the product differ if the temperature or time of heating is varied.

Uses.—Caramel properly prepared has an agreeable flavor well suited for confectionery, cakes, puddings, and ice cream. This use is obviously proper. The case is otherwise when it is added to colorless products, such as artificial vanilla extract, distilled vinegar, or liquors, to simulate a more valuable product or, to use the legal phraseology, make the product appear better or of greater value than it really is. Because of such fraudulent practices various tests have been devised for the detection of caramel, some of which are of questionable accuracy. Probably no other coloring matter commonly used in foods presents such difficulties in detection, and the extremely variable composition of different lots adds to the uncertainties.

CHEMICAL COMPOSITION.—Gélis¹ in his oft-mentioned investigation obtained, on heating, three distinct dehydration products of sucrose, namely: (1) *caramelan*, $C_{12}H_{18}O_9$, formed with a loss in weight of 12 per cent, soluble in 84 per cent alcohol; (2) *caramalen*, $C_{36}H_{50}O_{25}$, formed with a loss in weight of 14 to 15 per cent, insoluble in alcohol but soluble in cold water; and (3) *caramalin*, $C_{96}H_{102}O_{51}$, formed with a loss in weight of 20 per cent, insoluble in cold water.

Cunningham and Doree² found that, by heating sucrose as low as

¹ Ann 1858, [3], 52, 352; 1862, [3], 65, 496.

² J. Chem. Soc. 1917, 111, 589.

168° C. and with a loss of only 10 per cent, furfural, oily drops, and acid vapors, as well as water, were driven off, but the non-volatile residue, after heating at 170 to 180° C. until the loss was 12 per cent, was practically pure caramelan. Molecular-weight determinations showed that the formula should be $C_{24}H_{36}O_{18}$, or double that proposed by Gélis. The work of these authors indicates that caramelan is the first step in the anhydride formation and condensation, starting with simple sugars and leading to complex substances such as cellulose, humus, and caramelin.

Pictet and Andrianoff¹ by heating under diminished pressure (10 to 15 mm.) at 185 to 190° C. drove off successively one, two, and three molecules of water, the resulting products being, respectively: (1) *isosaccharosan*, $C_{12}H_{20}O_{10}$; (2) *caramelan*, $C_{24}H_{36}O_{18}$; and (3) *caramelen*, $C_{36}H_{50}O_{25}$. Isosaccharosan is precipitated from methyl alcohol by acetone as a white, amorphous, bitter, very hygroscopic, water-soluble powder melting at 94 to 94.5° C. The two other substances are identical with the caramelan and caramelen of Gélis.

Garino and Tosonotti,² recognizing that the three substances as prepared by Gélis by heating sucrose are mixtures, show how they may be purified. Caramelen is removed from caramelan by taking advantage of its solubility in 84 per cent alcohol; caramelen is separated from caramelin by cold water in which only caramelen is soluble. Glucic and apoglucic acids are formed when invert sugar is heated with caustic lime or other alkali. The color of caramelan solution is greatly increased by alkalies, and both caramelan and the calcium salt of glucic acid have marked surface activity.

Shumaker and Buchanan,³ who adopted the formulas for the three products given by Pictet and Andrianoff as noted above, observed that a foaming accompanies the time of removal of each molecule of water corresponding with each formula. They showed that the higher caramels are negative colloids stable in citric acid of pH 1.5, cold sulphuric acid of pH 1.5, and hot or cold phosphoric acid of pH 2 or 3, but precipitated by hot sulphuric acid of pH 1.5.

Minor Constituents.—Carles⁴ calls attention to the presence of *dextrin* in caramel made from glucose sirup and to various impurities in that made from molasses. Sucrose caramel is more uniform. He regards the presence of *sodium carbonate* as an adulteration. Garino-

¹ Helv. Chim. Acta 1924, 7, 703.

² Giorn. chim. ind. appl. 1929, 11, 8.

³ Iowa State Col. J. Sci. 1932, 6, 367.

⁴ Ann. chim. anal. 1910, 15, 305.

Canina,¹ on the other hand, demonstrated that addition of sodium carbonate during the heating of sucrose for the production of caramel increases the coloring, sweetening, and reducing power of the product.

Sangiorgi² states that although *formaldehyde* and *acetaldehyde* are produced during caramelization they oxidize completely to *formic acid* and *acetic acid* respectively. In commercial caramel he found on the average *furfural* 0.01, *acetone* 0.21, *formic acid* 0.16, and *acetic acid* 1.07 per cent. Simpson³ has shown that the amount of acetic acid formed during caramelization depends on the degree of caramelization, which in turn depends on the temperature and time of heating. Foods not heated above 160° C. should contain no formic acid. Caramel, according to Chapman,⁴ in addition to containing formaldehyde, may contain a substance responding to some of the tests for *benzoic acid*.

Drake-Law⁵ states that most of the reducing substances of caramel are volatile (aldehydes, etc.) and that dextrose is present only in small amount.

¹ Giorn. vinicolo ital. Oct. 1926; Notiz. chim. ind. 1927, **2**, 133.

² Giorn. farm. chim. 1913, **62**, 256.

³ Ind. Eng. Chem. 1923, **15**, 1054.

⁴ Analyst 1927, **52**, 215.

⁵ J. Soc. Chem. Ind. 1927, **46**, 428T.

PART II
ALKALOIDAL PRODUCTS

PART II

ALKALOIDAL PRODUCTS

INTRODUCTION

THE addiction to alkaloidal stimulants is world wide and dates back to prehistoric times. African natives chewed the cola nut, and the aborigines of Tropical America were acquainted with the stimulating properties of tobacco and the cocoa bean long before they came in contact with European civilization. Alkaloidal products containing morphine and some other potent alkaloids, obviously belonging in the category of drugs, also tobacco, are not described in this work. Most of those considered contribute flavor as well as stimulants and are consumed in conjunction with nutrients although, with the exception of cocoa, not themselves foods in the strict sense.

CHEMICAL CONSTITUENTS. Purine Bases.—See also Volume III, p. 276.

The active principles of the group are classed both as alkaloids and basic purines. *Caffeine* is the chief purine of tea, maté, coffee, and cola nut and one of the purines of cocoa. *Adenine* and *guanine* are present in tea. The relation of these and other bases of the group to *theobromine*, the chief purine and active principle of the cocoa bean, also to *barbituric acid* and the pyrimidine base *cytosine*, is brought out by the structural formulas on the next page.

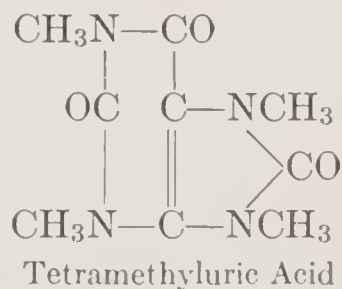
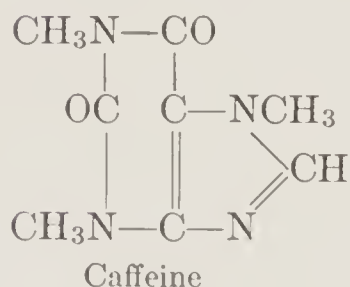
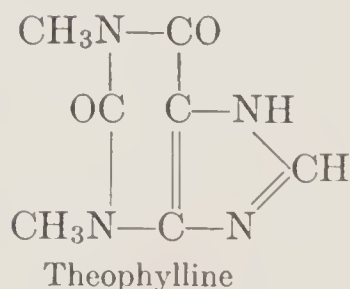
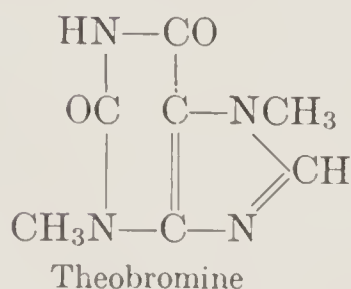
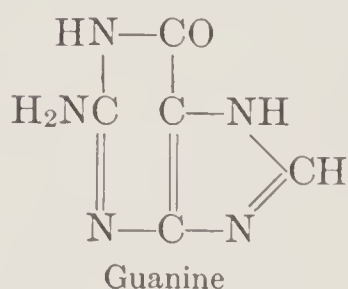
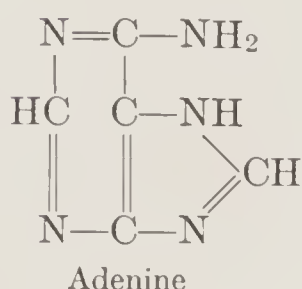
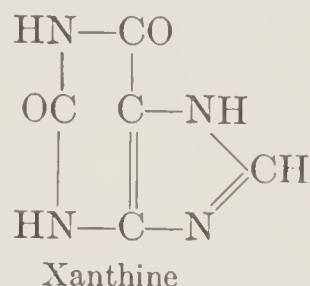
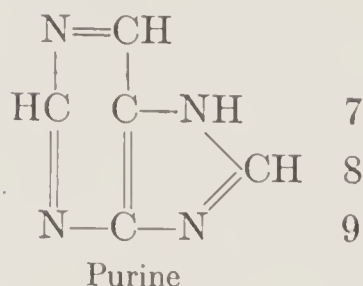
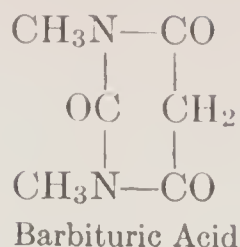
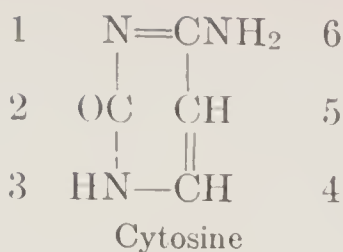
Caffeine, theine, or 1,3,7-trimethylxanthine, $C_8H_{10}N_4O_2 + H_2O$, was discovered in 1820 by Runge in coffee. Oudry¹ appears to have been the first to announce, under the name of theine, its presence in tea. Mulder² and Jobst,³ at the instance of Berzelius, established the identity of theine with caffeine.

The *preparation* of caffeine from coffee or tea involves processes similar to those used in its determination. Emil Fischer synthesized it from barbituric acid and from dimethylalloxan and by methylizing xanthine. It has also been prepared by methylizing theobromine and its isomer theophylline.

¹ Nouv. bibl. méd. 1827, 1, 477.

² Arch. Pharm. 1838, 65, 77.

³ Ibid. p 86.



The *properties* of caffeine follow: It forms long, silky, flexible, colorless, odorless crystals with a bitter taste. The crystals lose part of their combined water at ordinary temperatures and all of it at 100° C. The anhydrous substance melts at 235 to 237° C. It is soluble at 25° C. in 46 parts of water, 66 parts of alcohol, 5.5 parts of chloroform, and 530 parts of ether, also at 80° C. in 5.5 parts of water. With gold and platinum chlorides, caffeine forms double salts, and with the common inorganic acids and some organic acids it forms

normal salts. When caffeine is evaporated with chlorine water, yellow-red amalic acid is formed which with a small amount of ammonia water gives a purple color.

The maximum *medicinal dose* for humans is 0.5 gram. Various salts of caffeine are also used in medicine. Caffeine is the stimulating principle of certain proprietary sirups which, mixed with carbonated water, are dispensed in large quantities in the United States. The toxicity has been studied by Salant and Rieger.¹

Adenine, $C_5H_5N_5 + 3H_2O$.—This base was first isolated by Kossel² from the pancreas and other animal organs, and later from tea extract. Krüger³ found a considerable amount of adenine in tea. Calvery⁴ prepared from tea adenine nucleotide.

Crystals of adenine are needle-shaped. They become opaque on standing or more quickly by warming. The crystals are soluble in about 1000 parts of cold water, more soluble in hot water, somewhat soluble in hot alcohol, but insoluble in ether. When warmed with water, they show a characteristic cloudiness at 53° C.

Guanine, $C_5H_5N_5O$, occurs in animal organs, muscles, excrement (particularly of spiders), urine, yeast, tea, etc. It is a constituent of animal and vegetable nucleic acids.

It may be prepared as an amorphous powder or in minute crystals. It is insoluble in water, alcohol, and ether, difficultly soluble in ammonia, but dissolves in mineral acids, also sodium and potassium hydroxides.

Theobromine or 3,7-dimethylxanthine, $C_7H_8N_4O_2$.—The relation of theobromine to caffeine is shown by the constitutional formulas given above. This alkaloid forms fine white rhombic needles, subliming at 295° C. and melting at 329 to 330° C. It is soluble in 1600 to 1700 parts of cold and 100 to 150 parts of hot water, but is much less soluble in cold and hot alcohol and still less in ether. In dilute solutions of caustic alkalies it is quite soluble.

The substance together with caffeine may be extracted from a mixture of cocoa with calcined magnesia by boiling with water and filtering. The filtrate is evaporated to dryness, extracted with hot chloroform, and again evaporated. The residue after extracting the caffeine with cold benzol is theobromine. These operations carried out with certain precautions constitute the analytical method proposed by

¹ U. S. Dept. Agr., Bur. Chem. 1912, Bul. 148.

² Ber. 1885–1890.

³ Z. physiol. Chem. 1895, 21, 274.

⁴ J. Biol. Chem. 1926, 68, 593.

Decker.¹ It may be synthesized from lead xanthine and methyl iodide or from cyanacetic acid and methyl urea.

Theophylline or 1,3-dimethylxanthine, $C_7H_8N_4O_2 + H_2O$.—Kossel² isolated this isomer of theobromine from tea leaves.

The bitter white powder consists of crystals melting at $265^\circ C$. The crystals dissolve in 180 parts of cold water and are readily soluble in hot water. In alcohol and ether they are difficultly soluble. By methylizing the silver salt with methyl iodide, theophylline is transformed into caffeine.

Tetramethyluric Acid or Tetramethyltrioxypurine, $C_9H_{12}N_4O_3$.—Emil Fischer in 1884 synthesized 1,3,7,9-tetramethyl-2,6,8-trioxypurine, and Treat B. Johnson³ obtained it from the tea residue left after commercial caffeine had been extracted. It forms prisms and needles, both of yellowish color, melting at $225^\circ C$., very soluble in hot water and boiling chloroform, less so in alcohol, and only slightly so in ether. It is the first methyl derivative of uric acid and the fourth derivative of xanthine (the others being theobromine, caffeine, and theophylline) reported as occurring in a natural product.

Pyrimidine Bases.—*Cytosine*, $C_4H_5N_3C$, was first prepared by Kossel and his co-workers from thymus nucleic acid and synthetically by Wheeler and Johnson.⁴ It occurs in animal and vegetable nucleic acids. Calvery⁵ prepared cytosine from tea. Its structural formula is given above.

It crystallizes in thin scales, with a pearly luster, which are insoluble in ether and difficultly soluble in water and alcohol.

¹ Schweiz. Wochenschr. Pharm. 1902, **40**, 527, 541, 553.

² Z. physiol. Chem. 1888/9, **13**, 298.

³ J. Am. Chem. Soc. 1937, **59**, 1261.

⁴ Am. Chem. J. 1903, **29**, 503.

⁵ Loc. cit.

LEAVES OF THE COCA FAMILY

(*Erythroxylaceæ*)

THE only economic species of this family of any considerable importance is coca, a tropical plant long known in South America to contain a stimulant. Coca is now grown to a limited extent throughout the tropics.

COCA LEAF

Erythroxylon Coca Lam.

Fr. Feuilles de coca. Sp. Coca. Peru. Cuca. Braz. Ipadu.
Ger. Cocablätter.

The coca leaf is valuable chiefly because it contains, as its chief alkaloid, cocaine, which is both an invaluable local anesthetic and a dangerous habit-forming drug. South American Indians by chewing the leaves are said to be able to perform unbelievable muscular tasks with little nourishment, knowledge of which led to the use, now discontinued, of coca extract in non-alcoholic effervescent beverages.

MACROSCOPIC STRUCTURE.—The oval *leaves* are about the same size as tea leaves but differ in that they lack teeth and are blunt at the apex, although the midrib is extended as a short spine. A unique feature is the presence of two curved ribs without bundle tissues, extending from base to apex nearly midway between the midrib and margins. The petiole is only a few millimeters long.

MICROSCOPIC STRUCTURE.—The *upper epiderm* is composed of polygonal, rather thick-walled cells, the *lower epiderm* of cells of irregular contour, and stomata. Except over the midrib and the veins the cells of the lower epiderm are extended beyond the surface as warts. The ribs owe their rigidity to a group of collenchyma cells beneath the epiderm. Nevinny in his monograph¹ and authors of works on pharmacognosy give further details.

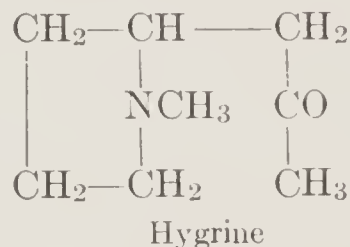
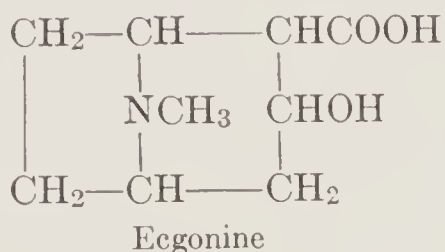
CHEMICAL COMPOSITION.—*Cocaine*, $C_{17}H_{21}NO_4$ or $C_8H_{13}-(C_6H_5CO)ON \cdot COOCH_3$, an ester, was discovered by Niemann,²

¹ Das Cocablatt, Vienna, 1866.

² Dis. Göttingen, 1860.

who separated it as monoclinic crystals. Soon after, Lossen¹ isolated *hygrine* ($C_8H_{15}NO$), a liquid, which later was found to consist of at least two substances, α - and β -*hygrine*. Later investigators have found the coca leaf a fertile field for research. Among the alkaloids related to cocaine the following have been isolated: (1) *cocamine*, *isotropylcocaine*, α -*truxilline*, or *truxillococaine* ($C_{28}H_{46}N_2O_8$); (2) *isococamine*; (3) *benzoylecgonine* ($C_{16}H_{19}NO_4$); and (4) *cinnamylcocaine* ($C_{19}H_{23}NO_4$). A tannic acid known as *cocatannic acid*, a substance related to quercetin, and waxy substances are also present. An important contribution to the subject is the monograph by Novy.²

Cocaine is hydrolyzed by acids into ecgonine ($C_9H_{15}NO_3$), benzoic acid ($C_7H_6O_2$), and methyl alcohol. The relationship of ecgonine to hygrine is shown by the following formulas:³



¹ Dis. Göttingen, 1862.

² Cocaine and Its Derivatives, Detroit, 1887.

³ Small in Gilman: Organ. Chem. 1938, 2, 1042. 1052.

LEAVES OF THE HOLLY FAMILY

(*Acquifoliaceæ*)

Ilex is the only genus of the holly family of economic importance. Although many of its species are grown for ornament and others are gathered for their bitter medicinal principles, maté and its closely allied species are the only ones used as food adjuncts.

MATÉ

Ilex paraguariensis St. Hil.

Fr. Maté. Sp. Té del Paraguay. It. Mate. Ger. Mate.

Maté is to South Americans what tea is to Orientals and coffee to Mohammedans. Special virtues have been claimed for the beverage by native writers and enthusiastic travelers. It is even stated that it wins out in a gastronomic contest with alcoholic beverages, and the cause of temperance is thus advanced without legislation. A gourd of maté is the token of hospitality offered to visitors in homes in Brazil, south of the Amazon, and countries to the south. Cups and spoons are not used, the drink being served in gourds or other flask-like vessels and imbibed through the *bombilla*, which is a tube fitted at the lower end with a strainer. In regions where modern ideas have taken root, the common *bombilla* and the common maté, as the gourd is known, are no longer passed from hand to hand and mouth to mouth, individual service being provided.

Species.—Common maté is the leaf of the above species, either wild or cultivated, but as in the case of coffee other species yield leaves containing caffeine which are used in the same manner as the true maté, as noted below.

Preparation.—The natives set up camp in a grove of maté trees where they gather and cure the leaves during a season of about six months. Commonly the ends of the branches are cut off, passed quickly through the flames of a fire to wilt the leaves, and dried on arbors over fires. The brittle leaves are beaten into fragments and

packed for shipment. A more modern process consists in plunging the leaves for a moment into hot water, drying over brick stoves, and reducing to fragments by machinery.

MACROSCOPIC STRUCTURE.—The obovate to elliptical-oblong leaves vary considerably in size and shape, but in general are 6 to 15 cm. long and up to 4 cm. wide, with rounded-pointed tip, short irregular teeth, and base narrowing to a short petiole. Both surfaces are dull and without hairs.

MICROSCOPIC STRUCTURE (Fig. 13).—Except in the ribs the tissues are (1) *upper epiderm* (*aep*) of thick-walled, polygonal, beaded cells with striated cuticle; (2) *palisade cells* in two, sometimes more, layers, passing into (3) mesophyl of *spongy parenchyma*, often with large intercellular spaces about which the cells are star-shaped; and (4) *inner epiderm* (*iep*²) of irregularly polygonal beaded cells, numerous stomata, and here and there water pores (*w*).

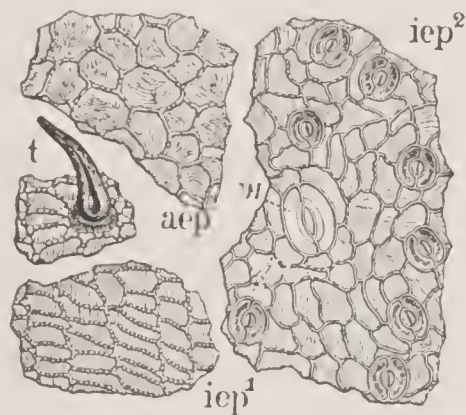


FIG. 13.—Maté. Leaf elements in surface view. *aep* outer epiderm; *iep*¹ inner epiderm over vein; *iep*² inner epiderm with stomata and *w* water pore between veins; *t* hair at junction of leaf blade and petiole. $\times 160$. (K. B. W.)

Over the ribs and veins the *epidermal cells* on both surfaces, particularly the lower (*iep*¹), are more or less quadrilateral, transversely elongated, and arranged side by side in longitudinal rows. Here and there certain epidermal cells are seen in cross section to be divided in half by cross partitions; Tschirch and Oesterle¹ note that the rounded inner portions of these contain mucilage.

Oil and oxalate clusters occur in the *mesophyl*.

Short, thick-walled *hairs* (*t*) occur at the junction of the leaf blade with the petiole.

The *fibro-vascular bundles* are encased in a sheath of numerous fibers, both thick- and thin-walled. The xylem elements are chiefly moderate-sized spiral vessels. Rows of rectangular pitted cells and cells containing oxalate rosettes (crystal fibers) are also present.

CHIEF STRUCTURAL CHARACTERS.—Leaves obovate to elliptical-oblong, toothed; petiole short.

Upper epiderm of thick-walled, polygonal, beaded cells; lower epiderm of irregularly polygonal cells, stomata, and water pores; short, thick-walled hairs at junction of leaf blade and petiole.

¹ Anat. Atlas, Leipzig, 1900, p. 265.

Histology of Other Species.—Cador¹ has made a study of the histological characters of the species of *Ilex* which are used or may be used in the preparation of maté. The species are herewith listed with numbers for ready reference in the key which follows the list:

South American Species: 1. *I. affinis* Gardn.; 2. *I. amara* (Vell.) Loes., a var. *longifolia* forma; 3. *I. chamædryfolia* Reiss.; 4. *I. cognata* Reiss.; 5. *I. congonhinha* Loes.; 6. *I. conocarpa* Reiss.; 7. *I. cuyabensis* Reiss.; 8. *I. diuretica* Mart.; 9. *I. dumosa* Reiss., a var. *montevidensis* Loes., b var. *Guaranina*; 10. *I. Glazioviana* Loes.; 11. *I. nigropunctata*, a var. *latifolia*; 12. *I. paltorioides* Reiss.; 13. *I. paraguariensis* St. Hil.; 14. *I. pseudothea* Reiss.; 15. *I. symplociformis* Reiss.; 16. *I. theezans* Mart., a var. *typica*, b var. *fertilis*, c var. *Riedellii*; 17. *I. vitis idæa* Loes.

North American Species: 18. *I. carolina* (Lam.) Loes.; 19. *I. Cassine* L., a var. *myrtifolia*; 20. *I. glabra* (L.) Gray; 21. *I. vomitoria* Ait.

CADOR'S KEY TO SPECIES OF ILEX

(Numbers refer to species in the foregoing list.)

- Upper epiderm one cell thick: 3, 4, 5, 6, 7, 8, 10, 12, 13, 15, 16a, 18, 19, 20.
- Upper epiderm two cells thick, at least in parts: 1, 16a, 16b.
- Upper epiderm with outer walls 30–40 μ thick: 14, 16a, 17.
- Upper epiderm with outer walls 12–24 μ thick: 1, 2, 3, 5, 6, 7, 8, 9, 10, 12, 15, 16b, 16c, 19.
- Upper epiderm with outer walls 6–9 μ thick: 4, 9b, 13, 18, 20.
- Upper epidermal cells in surface view with sinuous, pitted walls above, polygonal beneath: 4, 16a, 18, 19, 20.
- Upper epidermal cells in surface view with thin sinuous walls: 5, 9b.
- Upper epiderm strongly mucilaginous: 1, 2a, 5, 6, 11a, 15, 16, 18, 19a.
- Upper epiderm with mucilaginous cells here and there: 3, 10, 13, 14.
- Upper and lower epiderms with mucilaginous cells: 7, 9b, 20.
- Lower epidermal cells polygonal, thick-walled: 4, 8, 16a.
- Lower epidermal cells polygonal, thin-walled: 5, 7, 9b, 13, 16b, 16c, 18.
- Lower epidermal cells thick-walled, pitted: 6, 9a, 14, 19a.
- Lower epidermal cells thick-walled, more or less sclerenchymatized and pitted: 1, 2, 3, 10, 17.
- Lower epidermal cells with thin sinuous walls: 20; 19 (walls also sclerenchymatized and pitted).
- Upper cuticle striated: 4, 5, 6, 10, 12, 16b, 17.
- Upper and lower cuticle striated: 1, 2, 3, 7, 8, 9b, 13, 15, 18, 19a.
- Stomata with rod or wall-like thickenings: 2, 4, 6, 16a, 19a, 20.
- Cork warts on lower epiderm: 2, 5, 6, 8, 9a, 14, 15, 17.
- Hairs on upper epiderm: 14, 17, 19a.
- Hairs on upper and lower epiderm: 19.
- Palisade layer of short cells: 3, 4, 5, 6, 7, 9b, 10, 12, 15, 16, 17, 18, 19, 20.

¹ Dis. Erlangen, 1900.

Palisade layer of high cells: 1, 2, 9a, 13, 14.

Spongy parenchyma with large intercellular spaces: 1, 2, 3, 4, 6, 7, 9a, 9b, 10, 12, 13, 14, 16b, 17, 18, 19, 20.

Spongy parenchyma with small intercellular spaces: 3, 5, 8, 15, 16a, 16c, 19a.

Bundle of larger nerves with sclerenchyma sickle-shaped in cross section: 2, 3, 8, 10, 12, 16, 17, 18, 19, 20.

Bundle of larger nerves within sclerenchyma ring: 1, 5, 7, 9, 13, 14, 15.

Bundles with sclerenchyma above and below: 4, 6.

Oxalate clusters up to 30–60 μ : 1, 2 (45 μ), 3, 4, 5, 7, 8 (45 μ), 10, 15, 16b, 16c, 18, 19, 19a (60 μ), 20.

Oxalate clusters up to 15–21 μ : 6, 9b, 12, 13, 14, 16a, 17.

Caffeine reaction strong: 2, 4, 6, 9, 10, 12, 13, 14, 15, 16, 17, 18.

Caffeine reaction weak: 1, 5, 7, 19.

Caffeine reaction weak or none: 3, 8, 19a, 20.

In addition to species of *Ilex*, Loesner¹ states that the following are used for maté: *Coussarea hydrangeæfolia* Benth. et Hook., *Lomatia obliqua* R. et P. R. Br., *Rapanea guyanensis* Aubl., *R. lætevirans* Mez, *R. matensis* Mez, *Rudgea major* (Cham.) Müller, *R. myrsinifolia* Benth., *Symplocos caparoënsis* Schwarke, *S. lanceolata* A. DC., *S. variabilis* (Mart.) Miq.

CHEMICAL COMPOSITION.—Results of single analysis by Katz,² after removal of 26 per cent of stems, and by Bertrand and Devuyst,³ the range and average of 17 analyses by Rammstedt,⁴ the average of analyses by Hennings,⁵ and the range of 17 samples by Krauze⁶ are tabulated herewith:

COMPOSITION OF MATÉ

	Water	Protein*	Pure protein†	Caffeine	Fat	Tannin	Fiber	Total ash	Soluble ash	Water extract
	%	%	%	%	%	%	%	%	%	%
Katz.....	9.38	12.81	10.50	1.15	6.57	7.74	7.24	2.61	31.18
B. and D.....	10.50	13.31	9.69	2.02	11.22‡	5.98
Rammstedt:										
Min.....	7.18	13.18§	0.71§	34.20
Max.....	13.04	19.50§	1.56§	48.63
Aver.....	9.40	15.79§	1.19§	38.81
Hennings.....	9.00	13.56	9.75	2.10	7.75	9.80	15.45	6.62¶	2.26	33.10
Krauze:										
Min.....	6.90	0.58	7.80	6.09	35.27
Max.....	10.40	1.64	10.98	7.38	49.60

* Total N \times 6.25. † Total N less caffeine N \times 6.25. ‡ Sugar calculated as sucrose 6.08%
§ Dry basis. || Volatile ether extract 2.05; resin 9.10%. ¶ Alkalinity of ash calculated as K₂CO₃ 0.69; sand 3.26%.

¹ Ber. deut. phram. Ges. 1896, p. 203.

² Centralbl. Nahr. Chem. 1896, 2, 261.

³ Bul. sci. pharmacol. 1910, 17, 249.

⁴ Pharm. Zentralh, 1915, 56, 29, 708.

⁵ Ber. deut. phram. Ges. 1920, 30, 22.

⁶ Mitt. Lebensm. Hyg. 1932, 23, 218.

Peyer and Gstirner¹ report on 21 samples about the same range as Krauze. Their average for volatile oil was 0.08 and for fiber 20.40 per cent.

Cerioti² states that the following limits are proposed for adoption in Argentina: min. leaves 55, max. dust 20, max. stems 25, max. water 10, min. water extract 25, max. ash 8, max. ash insoluble in 10 per cent hydrochloric acid (sand) 2, and min. caffeine 0.70 per cent.

Relation of Grade to Composition.—Polenske and Busse³ analyzed 3 grades, I, young leaves with few ribs and stems, II, older leaves with more ribs and stems, and III, leaves with many ribs and stems, with results as follows:

	Water	Caffeine	Tannin	Ash	Water extract
	%	%	%	%	%
I.	6.79	0.88	9.59	6.00	36.66
II.	6.78	0.71	8.87	6.02	35.63
III.	6.98	0.53	8.10	5.44	34.13

CONSTITUENTS. Purine Bases. Caffeine.—The alkaloid of maté formerly known as matteine, has been shown to be identical with the caffeine of tea and coffee (see Introduction to Part II). Cappelli⁴ on careful search was unable to find any other alkaloid present.

Guglielmelli and Palet⁵ confirm Rammstedt's minimum results for caffeine and state that 1.25 per cent, the minimum limit proposed at the Paris White Cross Congress of 1909, is too high. Palet,⁶ however, shows that Stenhouse's earlier result, 0.13 per cent, was low owing to a faulty sublimation method. Brieger⁷ reports as high as 2.50 per cent, but this figure for maté, as well as those by the same chemist for tea and coffee, appears to be too high. Krauss, Kleucker, and Kolthath⁸ give 0.3 to 1.5 per cent as the range.

¹ Apoth.-Ztg. 1932, 47, 672.

² Rev. farm. 1927, 67, 3.

³ Arb. kais. Gesundh. 1898, 15, 171.

⁴ Ann. lab. Gabelle 1913, 6, 419.

⁵ An. soc. cien. Argentina 1915, 80, 246.

⁶ An. soc. quím. Argentina 1917, 5, 91.

⁷ Pharm. Zentralh. 1914, 55, 975.

⁸ Z. Unters. Lebensm. 1933, 66, 348.

Tannin.—Arata,¹ as a result of his studies, announced that the tannin of maté is not the same as that of tea and other common tannin-containing materials. Peckolt² describes two substances, mateviridic acid and matetannic acid; the former he claimed is crystalline, the latter amorphous. There is obvious need of further investigation.

According to Woodward and Cowland,³ maté contains caffetannin or a closely allied substance but no true tannin. The yellow color appears to be derived from flavone.

Astringent Principle.—After careful search J. C. and B. L. DeG. Peacock⁴ were unable to isolate any astringent substance other than a *phlobaphene* which was found to be combined with caffeine.

Various Constituents.—Hauschild⁵ identified in maté inactive *inositol*, *matésterol* ($C_{28}H_{46}O_3$), and a substance believed to be related to chlorogenic acid.

Mineral Constituents.—Katz⁶ made partial analyses of the total ash and the water-soluble ash of stem-free maté with results, calculated to air-dry maté, as follows:

	K ₂ O	CaO	MgO	Fe ₂ O ₃	Al ₂ O ₃	Mn ₃ O ₄	P ₂ O ₅	SO ₃	SiO ₂ *	Cl
	%	%	%	%	%	%	%	%	%	%
Total.	0.83	0.52	1.09	0.12	0.10	1.83
Soluble. . .	0.44	0.14	0.46	0.02	0.11	0.07	0.13	0.22

* Includes sand.

Hanausek⁷ states that the ash contains: K₂O 14.62, Na₂O 10.06, and Mn₃O₄ 8.96 per cent.

Minor Mineral Constituents. *Iron.*—Polenske and Busse⁸ in the grades described above found Fe₂O₃ plus Al₂O₃: I, 4.03, II, 4.21, and III, 3.00 per cent of the ash equivalent to I, 0.24, II, 0.25, and III, 0.16 per cent of the air-dry maté, indicating that the high percentages found by Katz were due to dirt.

¹ Jahresb. Pharm. 1878, p. 164.

² Z. allg. oesterr. Apoth.-Ver. 1882, 20, 257, 310.

³ Analyst 1935, 60, 135.

⁴ J. Am. Pharm. Ass. 1922, 11, 609.

⁵ Mitt. Lebensm. Hyg. 1935, 26, 329.

⁶ Loc. cit.

⁷ Nahr.-Genussm., Kassel, 1884, p. 394.

⁸ Loc. cit.

Manganese.—See above. Polenske and Busse in the 3 grades found Mn_3O_4 : I, 5.51, II, 6.45, and III, 5.90 per cent of the ash equivalent to I, 0.33, II, 0.39, and III, 0.32 per cent of the air-dry maté. Krauze,¹ in 17 samples, found, in the ash given in the table above, 1.88 to 4.26 per cent.

¹ Loc. cit.

LEAVES OF THE TEA FAMILY

(*Ternstroëmiaceæ*)

To this family belong tea and the closely allied camellias of the greenhouses.

TEA

Thea sinensis L. = *Camellia Thea* Link.

Fr. Thé. Sp. Té. It. Te. Ger. Tee.

Tea grows wild in Assam as a tree of considerable size with leaves somewhat larger than those of the shrubby form cultivated in China. Probably both belong to the same species, although Masters has assigned to the wild form the name *Thea assamica*. In China, tea has been grown for four thousand years or more, and any specimens found in the forests doubtless have escaped from cultivation. The shrub was introduced into Japan during the thirteenth century, into India, Ceylon, Java, and other parts of the East Indies toward the middle of the nineteenth century, and into South Carolina toward the close of that century. Today India and Ceylon lead in tea export, China having fallen far behind.

Before the processes of curing were known to Occidentals green and black tea were thought to be produced by different species, hence the names *T. viridis* L. and *T. bohea* L., which have been retained as designating well-marked Chinese varieties. Other varieties are *T. stricta* and *T. lasiocalyx*. Green tea is steamed to destroy enzymes and dried immediately after picking, thus retaining the chlorophyl; black tea differs from green tea merely in that the unsteamed leaves are fermented in heaps before drying. In both cases the leaves are usually rolled and until recently quite commonly faced to improve the appearance.

The common grades of Chinese tea are: flowery pekoe (leaf buds), orange pekoe (half-grown leaf), pekoe (first leaf), first-grade souchong (second leaf), second-grade souchong (third leaf), congou (fourth leaf), and bohea (inferior grade). Various subgrades and mixed grades are marketed. Chinese green teas are classed as young hyson, hyson, gunpowder, etc.

The designations basket-fired, pan-fired, and sun-dried are self-explanatory. Tea is often perfumed by mixing with fragrant flowers of the jasmine, gardenia, orange, etc.

Adulteration.—At the present time, in the United States at least, any form of tea adulteration is of such rare occurrence as to be negligible. European authors, a half century since, dilated on the presence of foreign leaves, exhausted leaves (the residue after preparing the beverage), and mineral weightings, but the present writers, who have examined hundreds of samples, beginning nearly fifty years since, recall only one instance where foreign leaves were present—the



FIG. 14.

FIG. 14.—Tea. Leaf, viewed from below. $\times 1$. (A.L.W.)



FIG. 15.

FIG. 15.—Tea. Immature fruit. $\times 1$. (A.L.W.)

amount being trivial—and no instance where there was evidence of spent leaves or mineral weighting. It is true that the facing of green tea with Prussian blue or ultramarine together with turmeric to produce a green color was formerly almost universal, but this practice, however senseless, was no more culpable than the coloring of butter.

MACROSCOPIC STRUCTURE.—The *leaf* (Fig. 14) varies in size with the variety and stage of development. Leaves of Chinese and Japanese varieties are somewhat narrower and more tapering than those of Indian and Ceylon varieties. All have short, irregularly distributed teeth, a sharp tip, short pedicel, a glassy surface, and veins joined by loops near the margins.

The *flowers* are seldom found in the commercial product. They have 5 short, rounded sepals, 5 white petals, and numerous stamens. The resemblance to cherry blossoms is quite close.

Immature tea *fruits* (Fig. 15) are sometimes present in tea. They are three-celled with a seed in each cell.

MICROSCOPIC STRUCTURE. **Interveinal Tissue** (Figs. 16 and 17).—Cutting through the thin part of the leaf the tissues are: *aep* upper epiderm with slightly wavy walls, *pal* palisade cells of the usual type, *mes* spongy parenchyma of the mesophyl with *cr* crystal cells,

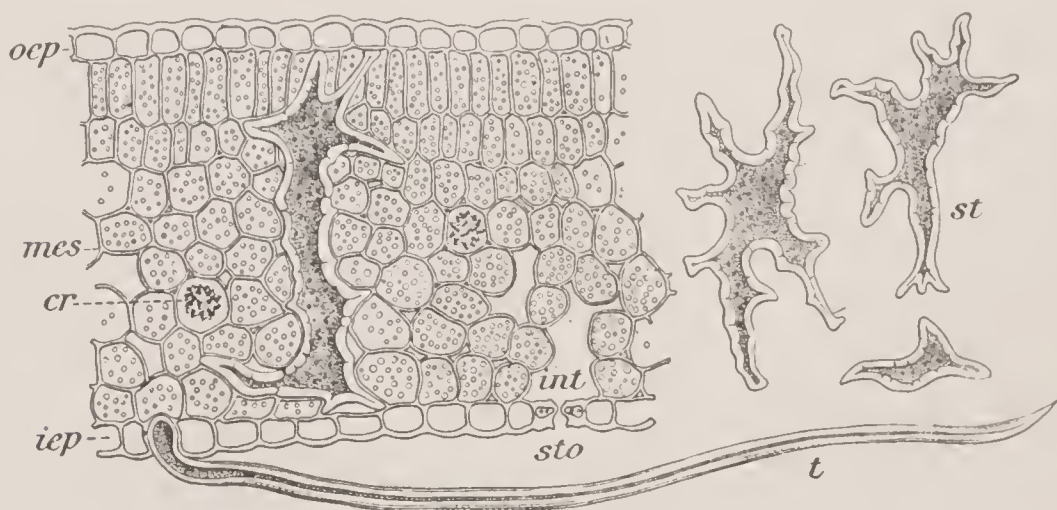


FIG. 16.—Tea. Leaf in cross section. *oep* upper epiderm; *mes* mesophyl with chlorophyl, stone cell, *cr* crystal, and *int* intercellular space; *iep* lower epiderm with *t* hair and *sto* stoma; *st* stone cells. $\times 160$. (A.L.W.)

also *st* and *st*¹ stone cells, and *iep* lower epiderm with *t* hair and *sto* stoma.

Chlorophyl grains occur in the palisade cells and spongy parenchyma. Both stone cells and hairs are highly characteristic.

The *stone cells* form, as it were, trusses between the two epidermal layers, the portion adjoining the lower epiderm often being broader than that adjoining the upper. Some have thin walls (Fig. 18, I); others (II), walls so thick as to reduce the lumen in parts to a mere line. Numerous pores are evident in the thick walls. The curious branching forms are particularly evident after removal of the adjoining tissues by maceration.

The *hairs* are slender, thick-walled, and pointed. At the base they are commonly bent like a cane handle.

Midrib and Veins (Fig. 17, central portion).—The *lower epiderm* (*iep*²) is of rectangular, beaded cells arranged in longitudinal rows. In the thin-walled tissue above and below the fibro-vascular bundle occur stone cells (*st*²) similar to those of the interveinal part of the leaf, but their elongation is transverse.

The *fibro-vascular bundles* in cross section show a beautiful fan-shaped structure surrounded by a starch sheath and within this a sheath of bast fibers (*f*). Xylem elements are in spreading rows separated by rows of thin-walled cells. They include spiral and reticulated vessels (*sp*, *ret*). Separated from the xylem by a curved band of cambium tissues are the phloem groups, which are accompanied by crystal fibers (*cr*¹).

CHIEF STRUCTURAL CHARACTERS.—Leaf glossy, ovate, pointed, toothed.

Mesophyl with branching stone cells; inner epiderm with slender hairs, bent at the base; rosette crystals occur in the mesophyl, and crystal fibers accompany the bundles.

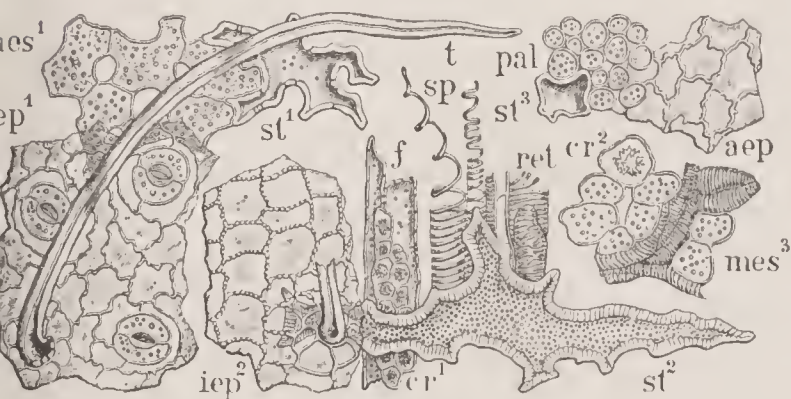


FIG. 17.

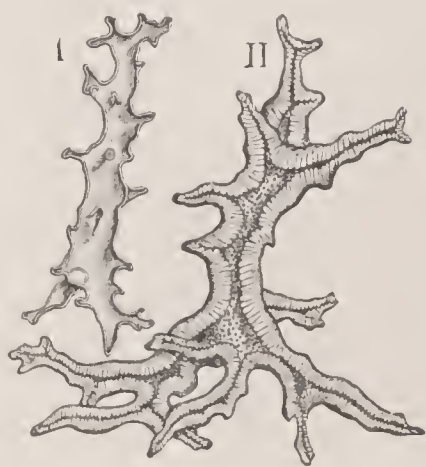


FIG. 18.

FIG. 17.—Tea. Leaf elements in surface view. Interveinal tissues: *aep* upper epiderm; *pal* palisade cells; *mes*¹ *mes*³ spongy parenchyma; *cr*² crystal cell; *st*³ top and *st*¹ bottom of vertical stone cell; *iep*¹ lower epiderm with *t* hair. Midrib tissues: *st*² transverse stone cell; *sp*. spiral vessel; *ret* reticulated vessel; *f* bast fiber; *cr*¹ crystal fibers; *iep*² lower epiderm. × 160. (K.B.W.)

FIG. 18.—Tea. Stone cells. *I* thin walls; *II* thick walls. × 160. (K.B.W.)

Moeller, Griebel, and other authors, including the writers in the *Microscopy of Vegetable Foods*, give much space to illustrations of the leaves of other plants showing the gross characters of the whole leaves and the minute structure of the epidermal tissues, as well as to explanatory text. Even if such foreign leaves were now added to tea, knowledge of the structure of the genuine leaf is adequate for detecting such frauds without resorting to a questionable system of plant analysis dependent on leaf characters alone, the number of species being limitless.

CHEMICAL COMPOSITION.—Pioneers among American chemists, whose analyses are given herewith, are Geisler¹ and Spencer, who in

¹ Am. Grocer Oct. 23, 1884.

1892 prepared Part 7 of Bulletin 13¹ containing analyses of samples from the open market. Mention in this connection should be made of Battershall, who examined numerous samples under the U. S. Tea Adulteration Act of 1883 and wrote an instructive chapter on tea in his work Food Adulteration and Its Detection. In addition to the constituents given in the table, Spencer determined total nitrogen, which varied from 2.91 to 4.58 per cent, equivalent to protein 18.19

COMPOSITION OF TEA

	Samples	Water	Caffeine	Tannin	Total ash	Soluble ash	Sand	Total extract	½ hour extract
		%	%	%	%	%	%	%	%
Geisler									
Green:	6								
Min.	4.69	1.52	11.87	5.89	2.02	0.21	43.30	30.20
Max.	7.78	2.68	19.11	8.91	5.02	0.66	50.00	44.70
Aver.	6.43	2.02	14.57	7.38	3.28	0.49	46.56	36.74
India:	6								
Min.	5.56	1.88	13.01	5.57	3.24	0.13	41.32	37.80
Max.	6.19	3.31	18.87	5.97	3.68	0.29	45.64	39.66
Aver.	5.81	2.70	14.87	5.81	3.52	0.19	42.92	38.77
Oolong:	13								
Min.	5.09	1.15	11.93	5.83	2.60	0.27	40.60	34.10
Max.	6.88	3.50	20.07	6.95	3.71	0.84	48.87	44.00
Aver.	5.89	2.32	16.38	6.32	3.20	0.51	43.32	37.88
Congo:	11								
Min.	7.65	1.70	8.44	5.75	2.28	0.32	27.48	23.48
Max.	9.15	2.87	13.89	7.79	3.52	1.31	37.06	32.14
Aver.	8.37	2.37	11.54	6.18	3.06	0.55	34.35	28.40
Spencer	63								
Min.	3.59	1.00	4.77	5.29	1.66	41.38	29.78
Max.	9.90	3.43	15.51	7.69	4.61	54.36	45.28
T. and T.									
India:	10								
Min.	5.30	2.78	13.32	5.22	2.84	0.04	43.47
Max.	8.20	4.91	16.61	6.55	3.91	0.46	49.75
Ceylon:	5								
Min.	5.60	10.13	5.14	2.76	0.03	41.32
Max.	8.00	13.91	5.48	3.27	0.05	48.25
China:	6								
Min.	6.12	7.27	5.93	2.92	0.08	38.43
Max.	9.06	10.94	8.87	3.61	2.74	46.94
Java...	1	7.54	3.40	14.48	5.88	3.50	0.13	44.84

¹ U. S. Dept. Agr., Div. Chem.

to 28.63 per cent. The analyses of tea on the English market, made by Tatlock and Thomson,¹ are more recent than those of the American chemists.

Among the more recent analyses are those by Pierotti² on 14 samples of commercial tea summarized herewith:

	Water 100° C.	Pro- tein	Theine	Tannin	Ether ext.	Carbon tetra- chlor- ide ext.	Chloro- form ext.	Dex- trin and gums	Cellu- lose	Ash	Water ext.
Min.	% 6.70	% 22.57	% 2.07	% 9.09	% 3.31	% 0.50	% 1.10	% 4.04	% 11.94	% 5.42	% 24.05
Max.	% 9.97	% 27.49	% 3.65	% 14.53	% 15.19	% 2.55	% 5.88	% 6.97	% 14.93	% 6.09	% 38.99

The literature is meager on ether extract and its constituents, proteins, soluble and hydrolyzable carbohydrates, and pentosans. Strangely enough, determination of crude fiber does not appear to be extensively employed in detecting an excess of stems, mechanical analysis being deemed sufficient.

In judging the purity of tea, the percentages of water extract in the tea and soluble ash in the total ash are deemed significant. The following summaries are of results by Beytheim and Bohrisch³ and Röhrig⁴ respectively: ash 5.3 to 6.4, aver. **5.8**, and 4.45 to 9.16, aver. **5.89**; water-soluble ash 2.1 to 4.0, aver. **3.1**, and 2.62 to 6.17, aver. **3.70**; water extract 29 to 45, aver. **35**, and 27.36 to 45.92, aver. **33.10**; soluble in total ash 33 to 68, aver. **54**, and 45 to 74, aver. **63** per cent.

Influence of Maturity on Composition.—Kellner, Makino, and Ogasawara⁵ analyzed the old (evergreen) leaves on May 15, also the young leaves on that date and twice monthly thereafter until November 30. Since the results increase or decrease quite uniformly, only those sufficient to show the trend are given herewith.

Machida⁶ compares the composition of "bud tea" and "coarse tea." The content of tannin, fiber, and hot-water extracts showed no significant differences, but the content of sugar was higher in the coarse tea.

¹ Analyst 1910, **35**, 103.

² An. soc. quím. Argentina 1918, **6**, 329.

³ Z. Unters. Nahr.-Genussm. 1900, **3**, 145.

⁴ Ibid. 1904, **8**, 730.

⁵ Landw. Vers.-Stat. 1887, **33**, 370.

⁶ J. Agr. Chem. Soc. Japan 1937, **13**, 569.

COMPOSITION OF TEA LEAVES AT DIFFERENT STAGES (KELLNER, ET AL.)
(Results on Dry Basis)

	Water when picked	Pro- tein	Pure pro- tein*	Caf- feine	Fat†	N-f ext.‡	Tan- nin	Fiber	Ash	Water extraet
	%	%	%	%	%	%	%	%	%	%
Old leaves:										
May 15.	60.03	16.56	15.19	0.84	14.18	46.50	11.11	17.62	5.14	36.45
Young leaves:										
May 15.	76.83	30.64	21.50	2.85	6.48	49.09	8.53	9.10	4.69	36.18
July 15.	72.67	20.06	14.44	2.51	7.00	49.49	9.40	19.16	4.29	31.72
Sept. 15.	65.26	18.27	14.19	2.05	13.40	44.35	11.32	19.13	4.85	30.01
Nov. 15.	59.43	17.70	14.38	1.29	20.38	38.66	11.34	18.26	5.00	38.21
Nov. 30.	60.97	17.14	14.69	1.00	22.19	37.29	12.16	18.34	5.04	37.91

* Total N less caffeine and amide N, times 6.25. † Ether extract. ‡ Includes tannin.

Influence of Method of Curing on Composition.—Remarkably in-
structive analyses by Kozai¹ show the changes induced during the
preparation of green and black tea.

COMPOSITION OF FRESH LEAVES, GREEN TEA, AND BLACK TEA (KOZAI)
(Results on Dry Basis)

	Pro- tein	Pure pro- tein *	Caf- feine	Fat †	N-f. ext.‡	Tan- nin	Fiber	Ash	Hot- water extract
	%	%	%	%	%	%	%	%	%
Fresh leaves	37.33	25.69	3.30	6.49	40.77	12.91	10.44	4.97	50.97
Green tea. . .	37.43	24.63	3.20	5.52	42.07	10.64	10.06	4.92	53.74
Black tea. . .	38.90	25.69	3.30	5.82	40.28	4.89	10.07	4.93	47.23

* Albuminoid N × 6.25. † Ether extract. ‡ Includes tannin.

Influence of Rolling on Solubility.—Sawamura² has found that
rolling not only accelerates the desiccation of tea during preparation,
as the result of pressing out the juice from the cells, but also increases
the solubility of the constituents. This is illustrated by the following
results obtained after heating 10 grams of the whole (not powdered)
sample at 100° C. for an hour, adding 200 cc. of boiling water, and
after 5 minutes' standing filtering through glass wool:

¹ Tokyo Imp. Col. Agr. 1889, Bul. 7, 24.
² 8th Int. Cong. App. Chem. 1912, 18, 313.

SOLUBLE CONSTITUENTS IN ROLLED AND UNROLLED GREEN TEA (SAWAMURA)

(Results in Parts per 100 of Each Constituent)

	Solids	Nitrogen	Theine	Tannin	Ash
Unrolled.....	22.12	18.23	61.07	25.85	24.19
Rolled.....	59.95	26.53	65.40	67.78	53.81

Influence of Firing on Quality and Composition.—Results by Sawamura¹ show that tea is improved in flavor by refiring, provided that the temperature of 70° C. is not exceeded for green tea and 80° C. for black tea. At these temperatures there is a slight loss of tannin, due probably to oxidation, but no appreciable loss of theine or in solubility, although at higher temperatures a decrease in tannin, theine, and solubility, as well as marked deterioration in color and flavor, were noted. Following are some of the results obtained:

COMPOSITION OF FIRED AND UNFIRED TEA (SAWAMURA)

	Water	In 100 Parts Dry Substance				
		Theine	Tannin	Solubility	Soluble theine	Soluble tannin
Green tea:						
Unfired.....	5.16	3.08	15.86	37.56	2.19	11.62
Fired at 80°...	3.17	3.21	15.42	36.46	2.54	11.71
“ “ 100°...	1.84	3.06	14.59	24.67	2.49	11.45
Black tea:						
Unfired.....	6.32	3.17	8.48	27.56	2.35	3.92
Fired at 80°...	3.22	3.15	7.40	27.10	2.41	3.98
“ “ 100°...	2.05	3.05	7.09	26.48	2.20	3.28

Stems.—While the wilful addition of worthless stems obviously degrades the product, Besson² combats the fixing of maximum limits since all Chinese teas have less than the proposed limit (22 per cent) and Ceylon teas contain over 70, India teas 60, and Java teas 50 per cent. Duess³ corroborates Besson’s conclusions and states that the

¹ Loc. cit.
² Chem. Ztg. 1915, 39, 82.
³ Chem. Weekbl. 1916, 13, 66.

more expensive grades actually contain more stems than the cheaper.

CONSTITUENTS. Proteins.—Shiratori¹ secured a Japanese patent July 21, 1920, for the manufacture of protein from tea for use in varnish, etc. The tea is heated with water at 70 to 80° for 6 hours, filtered, and the residue extracted with dilute alkali. The protein in the filtered extract is precipitated as brownish, odorless, and tasteless scales by neutralizing with acid.

Purine Basis. Caffeine.—See also Introduction to Part II, pp. 81 and 82.

St. Paul and Cownley² report the following limits for caffeine in tea on the dry basis: Ceylon 2.57 to 4.89, Indian 3.86 to 4.89, Chinese 2.42 to 3.78, Japan 2.60 to 2.93, and Java-Pecco 3.41 to 4.10 per cent. Other figures are given in foregoing tables. Van Romburgh and Lohmann³ give the following percentages of caffeine in parts of the tea plant grown at Buitenzorg, Java: first and second leaves 3.4, fifth and sixth leaves 1.5, hairs of young leaves 2.2, stem between fifth and sixth leaves 0.5, blossom leaves 0.8, green calyx 1.5, green pericarp walls 0.6, and ripe seed none.

Hartwich and Du Pasquier⁴ consider that caffeine results from the decomposition of proteins and exists largely in combination with tannin when picked, but during withering, rolling, fermentation, and roasting is liberated, as shown by the following results:

	Water	Total caffeine	Free caffeine	Combined caffeine	Tannin
	%	%	%	%	%
Pavia tea:					
When picked.....	75.27	4.24	0.58	3.66	29.70
Withered	43.64	4.23	1.55	2.68
Rolled	38.25	4.51	2.69	1.82	23.17
Fermented 2.5 hr. at 26° C.	35.57	4.11	2.72	1.39	17.26
“ 3.5 “ “ 46° C.	22.19	4.25	2.57	1.68	14.96
Roasted	9.67	4.27	3.20	1.07	12.59
Isola Madre tea:					
When picked	73.55	4.49	0.61	3.88	24.55
Fermented 4 hr. at 46° C...	32.96	4.41	3.87	0.54	21.00
Roasted	8.90	4.52	8.40

¹ Chem. Abs. 1921, 15, 2965.

² Pharm. J. Trans. 1887 [3], 18, 417; 1889, 20, 61.

³ Z. Unters. Nahr.-Genussm. 1898, 1, 213.

⁴ Apoth. Ztg. 1909, 24, 109, 119, 130, 136.

Duess¹ considers that the caffeine content bears no relation to the place or altitude where the tea is grown. He gives 3 per cent as the minimum for Java tea.

Adenine and *Guanine*.—See Introduction to Part II.

Calvery² separated guanine as nucleotide from tea leaves.

Tetramethyluric Acid, $C_9H_{12}N_4O_3$.—The structural formula and properties are given on pp. 82 and 84. It was isolated by Johnson³ from the by-product of the manufacture of caffeine from tea furnished by Carruth. It is the fourth methylated purine discovered in nature, the others being theobromine, caffeine, and theophylline. It is the only known natural methyl derivative of uric acid.

Fixed Oil.—Takei, Sakato, and Ōno⁴ found in the oil of fresh tea leaves the following acids: *acetic*, *propionic*, *butyric*, *valeric*, *caproic*, and *palmitic*, but in the oil of manufactured green tea chiefly *caproic*, *palmitic*, *heptoic*, and *o-methoxybenzoic*.

Child⁵ prepared *tea seed oil* by extraction with carbon tetrachloride and obtained the following values: specific gravity at 30° C. 0.914, refractive index at 30° C. 1.4674, saponification number 196.0, iodine (Wijs) number 88.7, acid number 0.83, thiocyanogen number (22 hr.) 76.3. It contained saturated glycerides including unsaponifiable matter 11.45, olein 74.25, and linolein 14.3 per cent.

Pritzker and Jungkunz,⁶ in 3 samples of *tea seed oil*, 1 each from Hongkong and Shanghai and 1 prepared by them from tea seed (100 grams seeds weighed 111.2 grams; water 10, protein 11.8, caffeine 0, fat 17.7, nitrogen-free extract 55.4, starch 14.2, fiber 2.4, ash 2.7 per cent; alkalinity of ash 81), found respectively: refractive index at 40° C. 1.4629, 1.4627, and 1.4639; saponification number 188.1, 187.7, and 190.4; iodine number 87.6, 87.5, and 89.6; acid number 2.2, 2.4, and 20.7; ester number 185.9, 185.3, and 169.7; Polenske number 1.3, —, —; and unsaponifiable matter 0.67, 0.68, and 1.31 per cent.

Further examination by Hilditch and Thompson⁷ convinced them that the *hexadecenoic acid* of the tea seed oil did not exceed 1 per cent of the total fatty acids.

¹ Chem. Weekbl. 1915, **12**, 938.

² J. Biol. Chem. 1927, **72**, 549.

³ Loc. cit.

⁴ Bul. Inst. Phys.-Chem. Res. (Tokyo) 1934, **13**, 1561.

⁵ Trop. Agr. (Ceylon) 1935, **84**, 71.

⁶ Z. Unters. Lebensm. 1935, **69**, 542.

⁷ J. Soc. Chem. Ind. 1937, **56**, 434.

Volatile Oil.—Early investigators reported 0.6 to 1.0 per cent of volatile oil, but Flückiger¹ found only a trace and Peckolt² none. Van Romburgh and Lohmann³ from 2500 kilograms of tea secured 130 cc. of volatile oil and from this 1.1 grams of *salicylic acid*, also *methyl alcohol*. *Acetone* was also believed to be present. Deuss⁴ was obliged to distil 1000 kilograms to obtain a sample sufficiently large for study. He separated two chief constituents: (1) an *alcohol*, probably with 6 C atoms, boiling at 156° C., and (2) *methyl salicylate* boiling at 220° C. Van Romburgh⁵ distilled 1 cc. of volatile oil from 15 kilograms of freshly fermented leaves. The principal fractions boiling between 154 and 158° C. were united and distilled under diminished pressure, yielding an alcohol ($C_6H_{12}O$) with boiling point under 28 to 30 mm. 75 to 80° C., specific gravity at 15° C. 0.8465, and refractive index at 19° C. 1.4376. Experiments indicated that the structural formula is probably $C_2H_5 \cdot CH : CHCH_2CH_2OH$. The same alcohol occurs in Japanese peppermint oil.

A yield of 0.014 per cent of volatile oil was secured by Takei and Sakato⁶ from fresh Spring leaves and of 0.007 per cent from fresh Summer leaves. From the oil *3-hexen-1-ol*, boiling at 157 to 158° C. (760 mm.), *α -naphthylurethan*, melting at 68° C., and *4'-iododiphenylurethan*, melting at 158° C., were prepared, hence their occurrence in black tea is not due to fermentation.

Green Tea.—The chief constituents of the volatile oil of green tea, according to Takei, Sakato, and Ōno⁷ are *α,β -hexenal* ($CH_3 \cdot CH_2 \cdot CH_2 \cdot CH : CHCHO$), *β,γ -hexanol* or *3-hexen-1-ol* ($CH_3 \cdot CH_2 \cdot CH : CH \cdot CH_2 \cdot CH_2OH$), and lower aldehydes which undergo changes, during fermentation, producing the characteristic odor of black tea. The same authors⁸ also isolated *iso-valeraldehyde*, *n-hexyl*, *benzyl*, and *benzyl-* and *phenyl-ethyl alcohols*, *phenol*, *cresol*, and *acetic* and *hexoic acids*, but no ester with the characteristic odor of the oil. They later⁹ found (1) *n-octyl alcohol*, (2) *geraniol*, and (3) an alcohol $C_5H_{12}O$, probably *β -methyl-butan- α -ol*. In the second paper they re-

¹ Pharmakognosie, Berlin, 1891, p. 649.

² Z. oesterr. Apoth.-Ver. 1884, **22**, 341, 360.

³ Z. Unters. Nahr-Genussm. 1898, **1**, 213; 1899, **2**, 290.

⁴ Chem. Weekbl. 1916, **13**, 692.

⁵ Proc. Acad. Sci. Amsterdam 1920, **22**, 758.

⁶ Bul. Inst. Phys.-Chem. Res. (Tokyo) 1933, **12**, 12.

⁷ Ibid. 1935, **14**, 303.

⁸ Ibid. 1935, **14**, 1262.

⁹ Ibid. 1936, **15**, 626; 1937, **16**, 7, with Sci. Papers Inst. Phys. Chem. Res. 1937 **13**, Nos. 671-675.

port, in addition to the foregoing: (1) *linaloöl*, (2) *acetophenone*, (3) *benzyl alcohol*, and (4) *citral-a*.

Black Tea.—The following were identified by Yamamoto and Kato ¹ in the steam distillate of Formosan black tea: *salicylic*, *phenylacetic*, *butyric*, *isovaleric*, and *palmitic acids*; from fractions of the concentrated ether extract they obtained *isovaleraldehyde*, *isobutyraldehyde*, *butyraldehyde*, α,β -*hexenal*, *phenylethanol*, *citronellol*, *geraniol*, β,γ -*hexanol*, *methyl salicylate*, and other substances not identified by them.

Yamamoto and Ito ² also distilled Formosan black tea and identified the constituents in the volatile oil separated from the distillate. Acid fraction: *propionic*, *isovaleric*, *caproic*, *hexenoic*, *caprylic*, *palmitic*, *benzoic*, and *salicylic acids* and *cresol*. Basic fraction: *quinoline*, *caproaldehyde*, *benzaldehyde*, *hexanol*, *hexenal*, *octanol*, *linaloöl*, *phenethyl alcohol*, *citronellol*, and *geraniol*.

Oxalic Acid.—Esbach ³ reports 0.38 per cent. According to Bau,⁴ water-soluble oxalic acid to the extent of 0.46 to 0.67 per cent is present. The amount of oxalic acid in the insoluble crystals of calcium oxalate was not determined. Arbenz ⁵ reports 1.43 per cent of oxalic acid in black tea, and Widmark and Ahldin ⁶ 1.39 per cent.

Ascorbic Acid.—Golyanitskiï and Bryushkova ⁷ determined the ascorbic acid content of fresh and dried tea leaves. The amount present varies with the location of the leaves on the plant. Although there is a great loss in manufacture, fermented leaves contain more than dried.

Tannin.—See also foregoing tables.

Analyses by Deuss ⁸ show that, although the leaf may contain 15 to 30 per cent of tannin, only 4 to 6 per cent usually passes into the aqueous extract. Carpenter and Harler ⁹ state that the fresh product contains 25 to 30 per cent of tannin which is reduced to about 15 per cent by fermentation. Dott ¹⁰ regards the percentage of tannin as a measure of astringency. Determinations by the copper acetate method

¹ Sci. Papers Inst. Phys. Chem. Res. (Tokyo) 1935, **27**, 122.

² J. Agr. Chem. Soc. Japan 1937, **13**, 736.

³ Bul. gén. therap. méd. chir. obstet. 1883, **104**, 407.

⁴ Z. Unters. Nahr.-Genussm. 1920, **40**, 50.

⁵ Mitt. Lebensm. Hyg. 1917, **8**, 98.

⁶ Biochem. Z. 1933, **265**, 241.

⁷ Compt. rend. acad. sci. U. R. S. S. (N. S.) **4**, 381.

⁸ Chem. Weekbl. 1916, **13**, 692.

⁹ Sci. Dept. Indian Tea Ass., Quar. J. 1922, Part 3, 99; Chem. Abs. 1924, **18**, 2022.

¹⁰ Pharm. J. 1933, **131**, 627.

gave: Indian tea, 2 samples, 19.43, 16.83; Chinese tea, 2 samples, 10.82, 9.36 per cent.

Harler¹ regards the seasonal variation of tannins as the most important factor influencing the color. High protein content increases the insolubility of the oxidized tannin. Large applications of nitrogenous fertilizers depress the tannin content.

Norman and Hughes² found a range of 9.5 to 16.8 per cent of tannin in 24 brands of tea, and Bagnall³ a range of 8.6 to 14.9 per cent in so-called tanninless tea. Norris⁴ discloses false claims of absence of tannin. Brands claimed to be tannin-free contained 14.1 to 16.2 per cent of soluble tannic acid, dry basis; those without such claims, 14.6 to 17.3 per cent.

Lamb⁵ found less *theotannin* in the buds of 4 Ceylon teas than in the first leaves and internodes.

Chemical Nature.—The tannin of tea was regarded by Hlasiwetz and Malin⁶ as identical with oak bark tannin. Prepared from tea by the Nanninga method⁷ it is stated by Deuss⁸ to be contaminated with a red impurity, while that prepared by his own method is white, although it oxidizes even when dry to a brown sirup. Results of analysis and molecular-weight determination point to the formula $C_{20}H_{20}O_9$. The author concludes that at least one CO group and eight OH groups are present, but that the COOH group is absent.

The same author records the following reactions: ferric chloride gives a black precipitate which is blue-black in very dilute solutions, lead acetate a yellow-gray precipitate, bromine water a yellow precipitate, and phenylhydrazine a yellow precipitate. Potassium permanganate oxidizes it completely with liberation of carbon dioxide; nitric acid decomposes it with formation of oxalic acid. It reduces Fehling's solution and ammoniacal silver oxide solution. When tea tannin is boiled for 6 hours with 5 per cent sulphuric acid, a red precipitate, stated to be similar to that formed with oak tannin, is obtained. Oak bark tannin is, however, an indefinite term, as the preparations of different investigators are not identical in composition or

¹ Quart. J. Sci. Dept. Indian Tea Ass. 1932, p. 101.

² Analyst 1936, **61**, 303.

³ Ibid. 310.

⁴ Schweiz. Apoth.-Ztg. 1936, **74**, 693.

⁵ Tea Res. Inst. Ceylon 1937, Bul. **17**, 60.

⁶ Z. Chem. 1867, **2**, 271.

⁷ Med. land. Plantentuin 1904, **46**, I, 23.

⁸ Rec. trav. chim. 1923, **42**, 496, 1053.

reactions, suggesting the presence of more than one substance. Etti prepared an oak bark tannin having the formula given above.

Deuss believes that the substance belongs to the group of condensed tannins since with bromine it yields a precipitate, with acids and by oxidation it forms an insoluble red-brown product, and, as stated by Freudenberg,¹ it does not react with the oxidizing enzyme of the leaf. He was not able, however, to decide whether or not the phloroglucinol radical, which is characteristic of the condensed tannins, is present in the molecule.

Tsujimura² groups as *catechols* or *catechins* substances with one hydroxylated ring attached to the double ring and as *tannins* those with two hydroxylated rings attached to the double ring (see structural formula below). His *tea catechol I* (melting point 237 to 238° C., specific rotation at 25° C. in alcohol -69°) corresponds to the anhydrous form of the *l-epicatechol* of Freudenberg and Purrmann;³ *tea catechol II* or *gallocatechol*⁴ had the same formula ($C_{15}H_{14}O_7$) and nearly the same melting point (218° C.) as the 5'-hydroxycatechol (227° C.) of Oshima and Goma⁵ and Oshima⁶ obtained by decomposing with hydrogen sulphide the lead acetate precipitate from the water extract of the fresh tea leaves, extraction with ethyl acetate, precipitation with chloroform, and crystallization in the cold of the hot-water solution. Oshima⁷ isolated from Formosan tea these two catechols, also an amorphous tannin identified as *bis-5,7,3',4',5'-pentahydroxyflavopinacol*.

Tsujimura⁸ obtained *tea tannin* ($C_{22}H_{18}O_{10}$) from green tea as a colorless amorphous powder which slowly oxidized in the air. Its specific rotation at 23° C. was -162.5° . By methylation, a derivative was obtained which, on oxidation, yielded trimethylgallic acid and veratric acid (dimethylprotocatechuic acid), thus showing a relationship of the tannin to pyrogallol ($C_6H_3(OH)_3$) and catechol ($C_6H_4(OH)_2$) respectively. The structural formula assigned by Tsujimura to tea tannin in his second paper, as given below, differs from that in his earlier paper merely in the arrangement of the single and double bonds of the conjugated rings.

¹ Chem. nat. Gerbstoffe 1920, p. 5.

² Sci. Papers Inst. Phys. Chem. Res. (Tokyo) 1929, **10**, 252.

³ Ber. 1923, **56B**, 1185; Ann. 1924, **437**, 274.

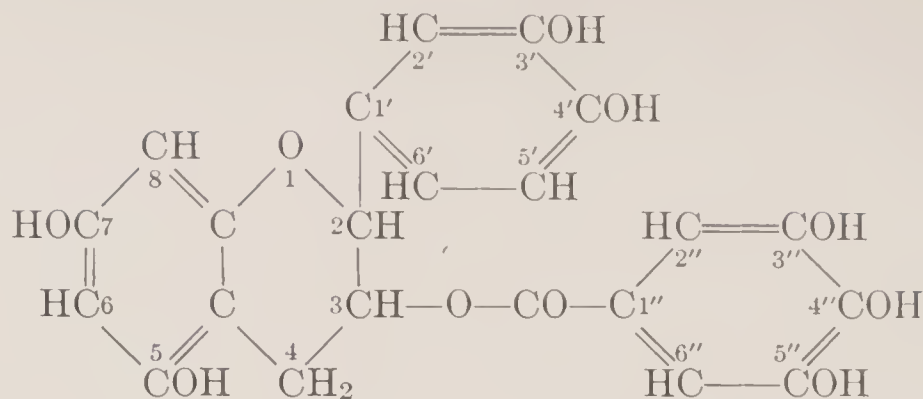
⁴ Sci. Papers. Inst. Phys. Chem. Res. (Tokyo) 1934, **24**, 149.

⁵ J. Agr. Chem. Soc. Japan 1933, **9**, 948.

⁶ Ibid. 1935, **11**, 750.

⁷ Proc. Imp. Acad. (Tokyo) 1936, **12**, 189.

⁸ Bul. Agr. Chem. Soc. Japan 1930, **6**, 70; 1931, **7**, 23.



Tea tannin (Tsujimura)

Later Tsujimura ¹ prepared tea tannin in crystalline form melting at 253° C. and with a specific rotation at 23° C. of -177.5° .

Yamamoto, Oshima, and Aima,² by a process similar to that followed later by Oshima and Goma, obtained in the lead precipitate a "tannin" as an amorphous powder with the melting point 85° C. and the specific rotation at 20° C. -129.7° , but in the filtrate from the lead precipitate they isolated crystals corresponding to Tsujimura's catechol I.

Nierenstein ³ gives a provisional formula for tea tannin and recognizes 2 tannases, namely, *3-galloyl-l-acacatechin tannase* and *gallo-tannase*.

Shaw and Jones,⁴ after reviewing the structural formulas proposed by Deuss and others, state their belief that theotannin, as prepared by extracting the fresh leaves with hot water, washing with benzol, saturating with sodium chloride, extracting with ethyl acetate, and precipitating with chloroform, is a variable mixture in which the aliphatic side chain attached to the quercetin skeleton is subject to change during growth. They ⁵ regard published figures for theotannin in black tea as unreliable and the hypothesis that in withering a sugar splits off from theotannin as untenable. The formation of caffeine theotannate is suggested as being the chief reaction.

Saponin.—From the ether extract of green tea, by extraction with hot 95 per cent alcohol and crystallization, Machida ⁶ obtained 0.08 per cent of a saponin ($C_{37}H_{58}O_{18}$) melting at 223° C. with decomposition.

¹ Sci. Papers Inst. Phys. Chem. Res. (Tokyo) 1935, **26**, 186.

² J. Agr. Chem. Soc. Japan 1930, **6**, 564.

³ Analyst 1936, **61**, 294.

⁴ United Planters' Ass. S. India Bul. 1935, No. 4a.

⁵ Ibid. No. 4b.

⁶ J. Agr. Chem. Soc. Japan. 1938, **14**, 301.

Colors.—*Quercitrin*, $C_{21}H_{22}O_{12} + 2 H_2O$, according to Deuss,¹ occurs in tea to the extent of about 0.1 per cent, the amount being independent of the method of preparation. The author has developed a test based on conversion into quercitin ($C_{15}H_{10}O_7 + 3 H_2O$).

Carotenoids.—From fresh tea leaves Yamamoto and Muraoka² isolated *carotene* 0.175 and *xanthophyl* 0.454 gram per kilo, melting at 174° and 192° C. and rotating $[\alpha]$ at 23° C. 361 to 380° and 341° in carbon disulphide respectively. Mackinney and Milner,³ who found optically active carotene in carrot leaves, state that this had previously been found only in tea and horse-chestnut.

Odor.—See also Volatile Oil.

Evidence submitted by Shaw⁴ supports the theory that the aroma is largely due to *oxytheotannin*.

Enzymes.—*Oxidase*, *diastase*, and probably enzymes affecting the flavor occur in tea. Sawamura⁵ states that in the manufacture of green tea oxidase is killed by steaming, otherwise the green color would not be retained. He recommends that the steaming be so regulated as to destroy the oxidase but not the diastase. In his experiments steaming 30 seconds accomplished this result.

Duess⁶ describes unpublished studies by Bernard and Welter on an oxidase of tea which is believed to be active during fermentation.

The oxidase present in tea was shown by Tatarskaya⁷ to act on phenols, pyrogallol, and hydroquinone, but not on guaiacol.

Lamb⁸ states that the activity of the principal oxidase increases with the increase of pH from 4 to 7. At higher pH, oxidation products of tannin interfere with the measurement.

Nikolaev and Shipsitina⁹ observed an increase of *peroxidase* up to 100 per cent in shaded leaves, activity reaching the maximum in the middle of the vegetative period, the maximum for *catalase* being at the end.

Mineral Constituents.—The composition of the ash of tea ("leaf") is a measure of mineral fertilizing elements removed by the crop; the

¹ Rec. trav. chim. 1923, **42**, 623.

² Sci. Papers Inst. Phys. Chem. Res. (Tokyo), 1932, **19**, 127; J. Agr. Chem. Soc. Japan 1932, **8**, 749.

³ J. Am. Chem. Soc. 1933, **55**, 4728.

⁴ Unit. Plant. Ass. S. India 1934, Bul. **8**.

⁵ Loc. cit.

⁶ Chem. Weekbl. 1923, **20**, 253.

⁷ Bul. Appl. Bot., Gen. Plant Breed (U.S.S.R.) 1936, Ser. III, No. 14, p. 135.

⁸ Loc. cit.

⁹ Arch. sci. biol. (U.S.S.R.) 1936, **43**, No. 1, 115.

composition of the infusion is a measure of what enters into the human organism. Below are averages of analyses of the ash of Oolong and Japan tea by Battershall¹ and of 3 samples of Java tea by Van Romburgh and Lohmann,² the results being in percentages of the ash (grams per 100 grams), also analyses by Kellner³ of the tea infusion recalculated to milligrams per gram of leaf. The three infusions A represent successive 5-minute periods of steeping, employing 180 grams of leaf per liter of water at 50° C., while infusion B represents only one period of 2 minutes' steeping, employing 100 grams of leaf per liter of water at 100° C. when added. These infusions are stronger than are ordinarily made for drinking; they furnish, however, a basis for calculation of the amounts in tea of any desired strength. It will be noted that the potash, soda, and magnesia are extracted from the leaf in relatively much greater proportions than the lime. The large proportion of chlorine found in the infusion is not consistent with the small percentage in the ash of the leaf. The presence of considerable manganese is noteworthy. Evidence as to the presence or absence of facing is lacking.

COMPOSITION OF ASH OF TEA LEAVES AND OF TEA INFUSION

	K ₂ O	Na ₂ O	CaO	MgO	Fe ₂ O ₃	Al ₂ O ₃	Mn ₂ O ₃	P ₂ O ₅	SO ₃	SiO ₂	Cl	CO ₂
Leaf:*												
Oolong. .	37.46	1.40	9.43	8.00	1.80	5.13	2.10	12.27	4.18	11.30	1.53	5.40
Japan. . .	41.63	1.12	8.18	5.33	1.12	4.26	1.30	16.62	3.64	9.30	1.60	5.90
Java. . . .	50.62	0.69	9.28	8.55	0.55	1.55	2.57	16.27	8.08	0.64	1.09
Infusion:†												
A 1st	2.97	0.86	0.06	0.68	0.22	0.15	0.65	1.03	0.38	1.81
A 2d	2.96	1.74	0.04	0.39	0.05	0.03	0.36	0.22	0.09	1.52
A 3d	1.20	0.27	0.03	0.29	0.03	0.02	0.28	0.20	0.06	0.13
B	13.84	1.01	0.34	1.42	0.22	0.48	2.33	0.80	0.04	0.69

* Results in grams per 100 grams of ash. † Results in mg. per gram of leaf.

Results by Deuss⁴ show a range of alkalinity of the ash from 70.2 to 90 cc. N acid per 100 grams of water-free tea and of soluble alkalinity from 86 to 153 per 100 grams of soluble matter.

The range in percentage of ash constituents of 14 commercial

¹ Food Adulteration and its Detection, London, 1887, p. 26.

² Z. Unters. Nahr.-Genussm. 1899, 2, 290.

³ Mitt. deut. Ges. Natur- Völkerkunde Ostasiens 4, No. 35; König: Chem. mensch. Nahr.-Genussm., Berlin, 1903, 1, 1016.

⁴ Chem. Weekbl. 1916, 13, 692.

samples, the composition of which by Pierotti appears earlier, is as follows:

	Alkalies	CaO	MgO	Fe ₂ O ₃	Mn ₂ O ₃	P ₂ O ₅	SO ₃	SiO ₂	Cl
	%	%	%	%	%	%	%	%	%
Min...	55.21	5.63	4.97	1.73	0.43	11.43	3.89	1.35	0.62
Max...	71.40	12.88	6.38	5.42	0.89	15.51	7.16	13.96	1.99

Lamb ¹ found 4.88 to 6.46 per cent of total ash and 3.21 to 4.37 per cent of soluble ash in normal teas grown in 4 districts of Ceylon, the higher percentages being in those grown at the lower elevations. Higher percentages of ash were present in the stems than in the corresponding leaves. Of the hard substance deposited from the tea juice on the tea-roller cap, 30 per cent was shown to be inorganic matter containing phosphates, iron, manganese, and other bases.

Minor Mineral Constituents. *Iron.*—Tea 140.5 to 163.2, aver. **154.6**; extract (100 grams) 5.5 to 9.5, aver. **7.2** mg. per kilo (Toscani and Reznikoff).²

Aluminum.—Ceylon tea 465 mg. per kilo, dry basis (Bertrand and Lévy).³

Manganese.—Tea 0.02 to 0.78 per cent, dry basis (Deuss).⁴

Iodine.—Japanese tea, 10 samples, 0.45 to 1.2γ per gram, dry basis; young leaves more than old; 33 to 75 per cent soluble in hot water (Itano and Tsuji).⁵ Kongo tea, 350 to 363; 10 per cent extract (100 grams) 164γ per kilo (Mayrhofer, Schneider, and Wasitzky).⁶

Fluorine.—Kongo tea 580 to 600; 10 per cent extract (100 grams) 380γ per kilo (Mayrhofer, Schneider, and Wasitzky).⁶ Large number of Chinese teas 15 to 1758 (maximum from fluorite region) mg. per kilo; a 2 per cent infusion extracted 81 to 96 per cent (Reid).⁷

¹ Tea Res. Inst. Ceylon 1937, Bul. **17**, 60.

² J. Nutrition 1934, **7**, 79.

³ Compt. rend. 1931, **192**, 525.

⁴ Loc. cit.

⁵ Proc. Imp. Acad. (Tokyo) 1935, **11**, 141.

⁶ Biochem. Z. 1932, **251**, 70.

⁷ Chinese J. Physiol. 1936, **10**, 259.

SEEDS OF THE PALM FAMILY

(*Palmaceæ*)

THE betel palm, in addition to various technical products, yields an alkaloidal nut used in medicine and for chewing.

BETEL NUT

(*Areca Catechu* L.)

Fr. Noix de bétel. Sp. Areca. Ger. Betelnuss.

Throughout southern Asia betel chewing is a common habit. The preparation used consists of leaves of *Piper Bètle* L., lime, and pieces of the betel nut. As in tobacco chewing, the saliva becomes colored, but in this case the color is deep red, not brown.

MACROSCOPIC STRUCTURE.—The *seed* is rounded-conical, 2 to 2.5 cm. long, gray-brown with spiral red veins. It consists largely of hard endosperm of the ruminating type similar to that of the nutmeg. The depressions on the surface between the deep wrinkles are filled by perisperm tissues, and the whole is enclosed in a thin spermoderm. The embryo is minute.

MICROSCOPIC STRUCTURE.—The cells of the endosperm are thick-walled, porous, and contain aleurone grains. The tissues between the wrinkles are dark brown with spirally thickened cells.

CHEMICAL COMPOSITION.—The principal alkaloid, *arecoline* ($C_8H_{13}NO_2$), was discovered by Bombelon, who gave it the name arecan. Jahns¹ further studied this alkaloid and three others isolated by him, namely *arecaidine* ($C_7H_{11}NO_2 \cdot H_2O$), *guvacine* ($C_6H_9NO_2$), and *arecaine* ($C_7H_{11}NO_2 \cdot H_2O$).

The nut also contains considerable *tannin*, *fixed oil*, and *color*.

¹ Ber. 1888, 21, 3404; 1890, 23, 2972; 1891, 24, 2615; 1892, 25, 198.

SEEDS OF THE SOAPBERRY FAMILY

(*Sapindaceæ*)

TREES and shrubs of this family yield a number of valuable tropical fruits, and a woody climber yields guarana, a caffeine-containing seed.

GUARANA

Paullinia Cupana Kth. = *P. sorbilis* Mart.

Fr. Guarana. Port. Guarana. Ger. Guarana.

The aborigines of South America, long before the discovery of the Western Hemisphere, were acquainted with the stimulating properties of guarana. Its use is now restricted to regions south of the Amazon and has largely given place to tea and coffee. The seeds are ground, roasted, made into a paste, and marketed in the form of cylinders about the size of rolls of brimstone. From these is prepared a beverage. Guarana is also used in medicine, and its properties are described in the U. S. Pharmacopœia.

MACROSCOPIC STRUCTURE.—The ovoid pointed *fruit* usually contains a single flattened, globular, brownish black *seed* about 1 cm. in diameter, with a small aril at the base. The embryo with its two thickened cotyledons is enclosed in a hard spermoderm.

MICROSCOPIC STRUCTURE.—The **Spermoderm** consists of (1) an *outer epiderm* of thick-walled palisade cells, (2) a *ground tissue* of parenchyma with stone cells occurring singly or in groups, and (3) a characterless *inner epiderm*.

Embryo.—The cells of the *cotyledon* contain small starch grains, often united to form twins, or triplets up to 25 μ in diameter. On treatment with alkali, needle-shaped crystals, believed to be caffeine, separate.

CHEMICAL COMPOSITION.—Several authors report about 5 per cent of *caffeine*. The content of *tannic acid* is variously stated as being from 5 to 10 per cent. Reliable figures on the percentage of *starch* are not available, but the content is believed to be less than 10 per cent. No figures on the content of *nitrogen* are at hand.

SEEDS OF THE STERCULIA FAMILY

(*Sterculiaceæ*)

THE cocoa bean and the cola nut, both products of trees of this family, owe their stimulating properties to two alkaloids, theobromine and caffeine. Other members of the family are ornamentals.

CHOCOLATE AND COCOA

Theobroma Cacao L.

Fr. Cacao. Sp. Coco. It. Cacao. Ger. Kakao.

Although small trees of several American species of the genus yield seeds of much the same character, the above species is the only one of considerable importance. Before the advent of Europeans the seeds were gathered by the aborigines of Mexico and Central and South America. Today the cocoa beans of commerce come largely from countries bordering on the Caribbean Sea, Brazil, French and British West Africa, and the East Indies.

The large gourdlike fruits, curiously enough, grow out singly from the trunk of the tree. Other striking features are the fragrant red flowers and the large dark green leaves. The seeds, freed from the adhering pulp, are sun-dried either immediately or after being subjected to a fermentation, continuing for several days, that improves the flavor.

Chocolate and Cocoa.—The beans are freed from stones and other impurities by sifting and roasted by a process similar to that employed for coffee, thus developing the characteristic flavor. After crushing, the shells are separated from the crushed cotyledons or nibs. Some manufacturers also remove the minute radicles known in the trade as “germs.”

Chocolate consists of ground cocoa nibs. The heat of grinding causes the fat to melt, and the mass is converted into a thin paste which is poured into molds. *Sweet Chocolate* is a homogeneous solid mixture of chocolate, sugar, and vanilla or other flavor; *Milk Choco-*

late consists of the same ingredients as sweet chocolate with milk powder in addition.

Cocoa is chocolate from which a portion of the fat (cocoa butter) has been removed by pressure when hot. In preparing the beverage it is desirable to produce as perfect an emulsion as possible. The more common means of accomplishing this is to pulverize the cocoa finely so that on boiling the particles remain in suspension in the paste formed by the gelatinization of the starch. The means resorted to in producing Dutch process cocoa is the addition of alkali during manufacture. Cocoa thus treated is darker but no more soluble than

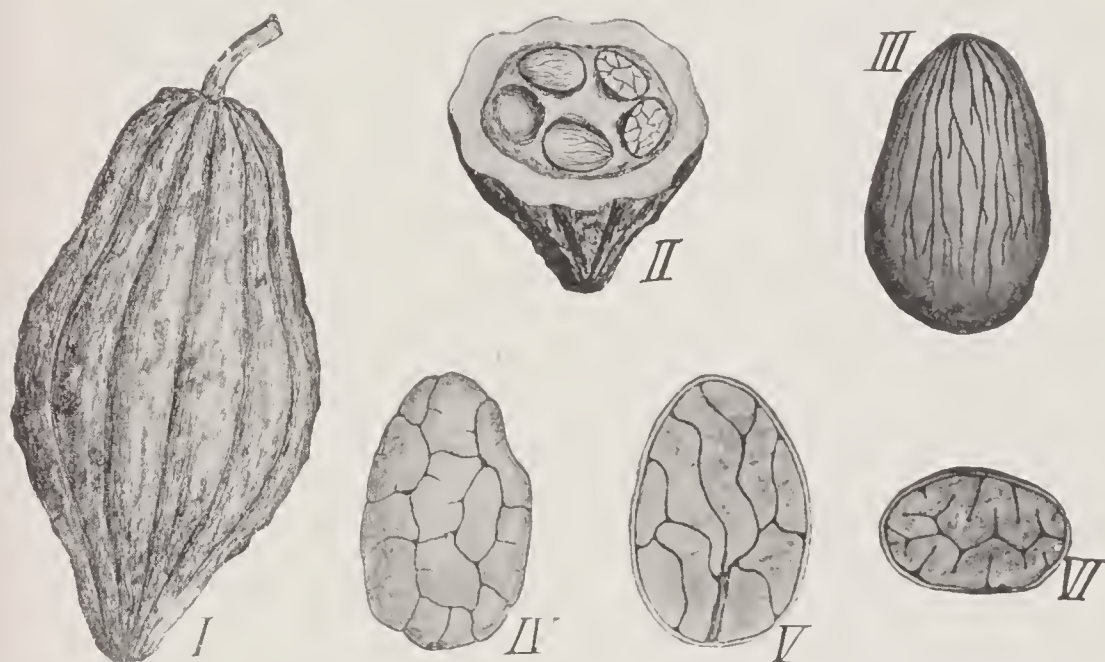


FIG. 19.—Cocoa. *I* entire fruit; *II* fruit in cross section, $\times \frac{1}{4}$. *III* seed; *IV* seed deprived of spermoderm; *V* seed in longitudinal section, showing radicle; *VI* seed in cross section. $\times 1$. (A.L.W.)

the ordinary product. Opinion is divided as to the relative excellence and wholesomeness of the ordinary product and Dutch process cocoa.

MACROSCOPIC STRUCTURE (Fig. 19.)—The yellow or brown *cocoa fruit* is from 12 to 18 cm. long, 5 to 9 cm. wide, and has 10 ridges passing from the base to the apex, giving the surface a melon-like appearance (*I* and *II*). It contains from 35 to 75 seeds in 5 rows, embedded in a mucilaginous substance.

Cocoa beans (*III–VI*) as found on the market consist of the anatropous *seeds*, often with more or less of the pulpy inner pericarp adhering. They are irregularly ellipsoidal, 15 to 30 mm. long, somewhat flattened, and vary from reddish brown to dark brown in color. The hilum at the broader end and the chalaza at the narrower end

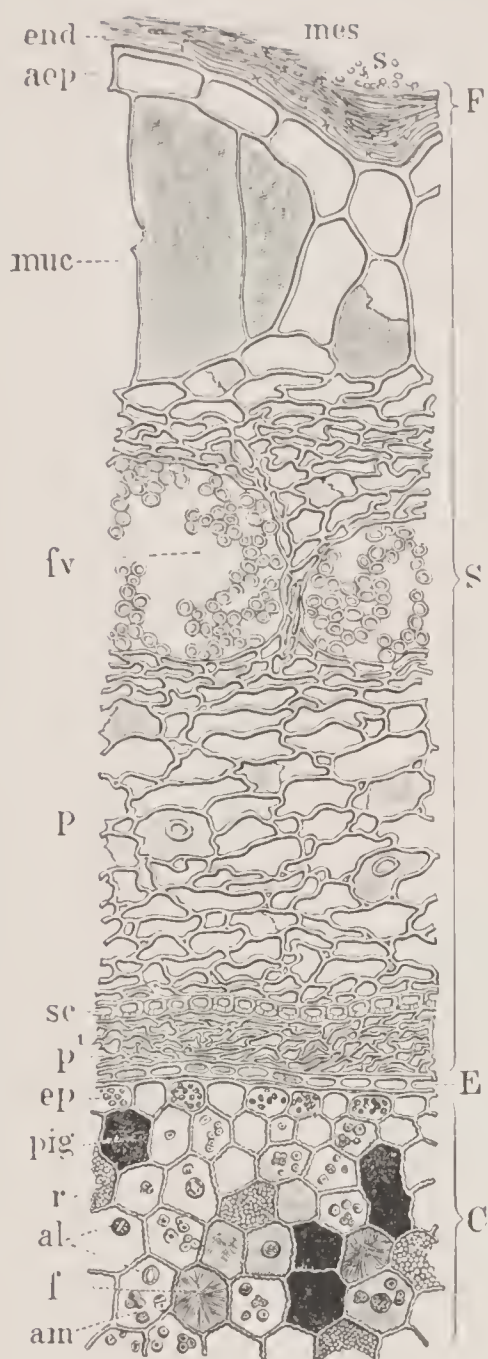


FIG. 20.—Cocoa. Bean in cross section. *F* adhering pericarp tissues: *mes* pulp cells with *s* yeast cells; *end* endocarp. *S* spermoderm: *aep* outer epiderm; *muc* mucilage cells; *p* spongy parenchyma with *fv* bundle of raphe; *sc* stone cell layer; *p*¹ inner parenchyma. *E* endosperm. *C* cotyledon: *ep* epiderm; *pig* pigment cells; *r* reticulated walls; *al* aleurone grains; *f* fat crystals; *am* starch grains. $\times 160$. (A.L.W.)

are connected by the raphe, which runs along one of the narrow sides and divides into numerous branches at the chalaza. The so-called "shell," consisting of spermoderm with portions of the inner pericarp adhering to the outer surface and the endosperm to the inner surface, is thin and brittle, readily breaking away from the cotyledons. There is no fleshy endosperm, the reserve material being entirely in the chocolate-colored embryo consisting of the two thick and curiously folded cotyledons and a hard, slender radicle about one-third the length of the seed situated at the helium end.

MICROSCOPIC STRUCTURE (Figs. 20, 21, and 22).—The **Pericarp** is represented by a small amount of collapsed cells of the *mesocarp* (*mes*), often with yeast cells (*s*) remaining from the fermentation, also elongated thin-walled, diagonally arranged cells of the *endocarp* (*end*).

Spermoderm (*S*).—The tissues are: (1) *outer epiderm* (*aep*) of large, thin-walled cells, often arranged end to end in longitudinal rows; (2) *mucilage cells* (*muc*) forming a series of large oval pockets divided by radial walls into large daughter cells; (3) *outer spongy parenchyma* (*p*) through which run fibro-vascular bundles (*fv*) of the raphe; (4) *stone cells* (*sc*) up to $25\ \mu$ in surface view with thickened and beaded inner and radial walls; and (5) *inner parenchyma* (*p*¹) of more or less collapsed small cells without distinctly differentiated inner epiderm.

Particularly noticeable are the narrow spiral *vessels* (*sp*) of the raphe which in the ground shells form a characteristic tangle.

Endosperm (*E*).—This is known as the silver skin. It surrounds the cotyledons and penetrates between the folds. The only well-defined layer is one of polygonal cells with thinner walls than those of typical aleurone cells. Tschirch and Oesterle¹ state that these cells contain crystals of fat and fatty acid, sometimes also oxalate crystals, while the tissues that extend between the cotyledons consist of obliterated inner layers. Usually the contents are indistinct and there is

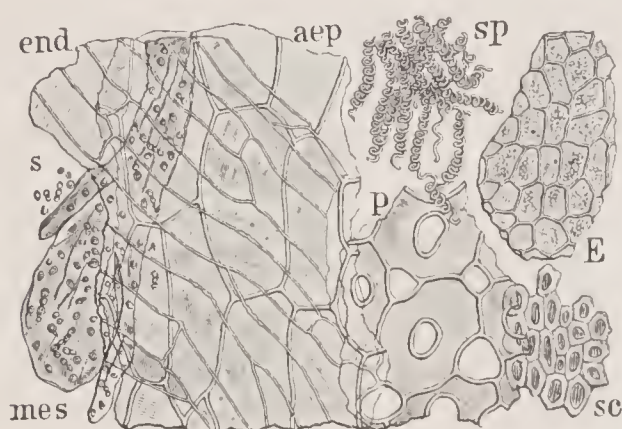


FIG. 21.



FIG. 22.

FIG. 21.—Cocoa. Elements of shell in surface view. *sp* spiral vessels of raphe bundle. Other reference letters as in Fig. 20. $\times 160$. (A.L.W.)

FIG. 22.—Cocoa. Surface view of *epc* epiderm of cotyledon and *epr* epiderm of radicle with *t* hair. $\times 160$. (A.L.W.)

reason to believe that they are much like the protein and fat of typical aleurone cells.

Embryo.—The remarkable *hairs* (*t*) occurring on both cotyledons (*C*) and radicle, particularly the latter, were first described by Mitscherlich.² They are short, blunt, and multicellular and often adhere to the endosperm. The three shown in Fig. 22 on the upper left of *epr* were cemented together. Other than these hairs, the *epiderms* of the cotyledons (*epc*) and radicle (*epr*) are characterless. Both the hairs and the other epidermal cells contain minute brown bodies up to $6\ \mu$.

Of paramount interest are the contents of the ground tissue cells of the cotyledon since these include practically all the valuable constituents of the seed—fat, starch, proteins, color, alkaloids, and flavoring constituents. In cross section, particularly when stained with chlorzinc iodide after extraction of the fat, the cell walls of the ground

¹ Anat. Atlas, Leipzig, 1900, p. 21.

² Der Cacao and Die Chocolate, Berlin, 1859.

tissues appear beaded where they stand upright and reticulated where the surface is exposed as in Fig. 20, *r*.

Fat (Fig. 20, *f*).—The most abundant constituent, making up 50 per cent by weight of the seed, forms the matrix in which the aleurone and starch grains are embedded. Usually it appears to be amorphous, but in glycerin mounts may show crystalline structure radiating from the center of the cells. Aleurone grains and starch are viewed after dissolving the fat by successive treatments with alcohol and ether.

The *aleurone grains* (Fig. 20, *al*), if indeed bodies some of which are not colored yellow with iodine in potassium iodide may be so denominated, vary up to 10 μ in diameter, the larger grains containing either one or more crystals or crystalloids or else several globoids. These larger grains are about the size of the larger starch grains.

Starch (Fig. 20, *am*).—The starch grains, as in other seeds, increase in size from without inward, reaching 12 μ . The smaller grains often occur in small aggregates. A distinct hilum is usually evident even in the smallest grains. By staining with iodine in potassium iodide the starch grains are readily distinguished from the aleurone grains.

Pigment Cells (Fig. 20, *pig*).—These are the seat of the cocoa-red and cocoa-brown further considered under Chemical Composition. Usually the contents form a purple or brown mass apparently filling the entire cell, although sometimes the contents are only faintly colored. To what extent this color is due to fermentation on standing, the evidence is conflicting. Although the color reactions as well as the color differ with the sample, in general, concentrated sulphuric acid gives blood red and sodium hydroxide green-yellow. With ferric chloride the color may be blue-black or, as noted by Hartwich,¹ red. Ferric chloride solution as ordinarily prepared is acid, hence a red color would indicate that only an acid (not an iron-tannin) reaction takes place.

The significance of these color changes, particularly those which are the resultant of two mixed colors, such as purple due to red and blue and green due to blue and yellow, awaits the time when we know more of the primary substances present in the beans and the changes brought about by ripening, sweating, drying, and exposure.

Hartwich² gives dimensions of different varieties of beans and the

¹ Arch. Pharm. 1887, **25**, 958.

² Handb. Nahrungsm.-Unters. Leipzig, 1915, **2**, p. 329.

starch grains, also the colors and reactions of the pigment masses. In the writers' opinion these data, so far as they refer to histological characters, are of value chiefly as showing the variation of the cocoa bean in general and do not represent fixed characters of individual commercial varieties. For example, Hartwich¹ states that Puerto Cabello beans do not contain the violet pigment, whereas we find that pigment in a sample examined by us. Again in Accra beans he finds the violet pigment, whereas in one sample we find no color and in another a brown pigment. As regards size of starch grains, Hartwich reports in Trinidad and La Guayra, respectively, maximum limits of 6 and 4 μ , whereas our measurements are 12 and 9 μ . It thus appears that in the case of the cocoa bean, as well as of many other seeds, certain histological and chemical characters are fixed, being inherent in the species, whereas others are variable, the variation being more often attributable to external conditions such as season, stage of development, curing, etc., than to the variety.

CHIEF STRUCTURAL CHARACTERS.—Shell papery, largely spermoderm with raphe and branches to which adhere traces of fruit pulp without and the silver skin or endosperm within. Cotyledons fleshy, convoluted; radicle short, slender.

Shells characterized by numerous spiral vessels of raphe and small beaker-shaped stone cells. Epiderm of cotyledons with short, fleshy, multicellular hairs. Aleurone grains and starch grains, both up to 12 μ , embedded in fat. Starch grains with distinct hilum; large grains rounded, small grains often in aggregates. Pigment cells purple or brown, changing to red with acid, or colorless.

CHEMICAL COMPOSITION. Cocoa Nibs and Shells.—On the following pages are analyses or summaries of analyses made by Winton, Silverman, and Bailey² by methods which for the most part were afterwards adopted by the Association of Official Agricultural Chemists. The first two tables show the composition of the nibs and corresponding shells of different varieties of cocoa beans sampled from original packages of New York importers. The analyses of the nibs show also the composition of plain chocolate or chocolate mass of known purity as this differs from cocoa nibs merely in mechanical condition.

Seven of the samples were different grades of Venezuelan or Caracas beans, the commercial designations and relative values as indi-

¹ Ibid. pp. 327–335.

² Connecticut Agr. Exp. Sta. Rep. 1902, pp. 248, 265, 270; Rep. 1903, p. 123.

cated by the quoted prices per pound (1902) being as follows: Chuao (33 ct.), Selected Venezuelan (32 ct.), San Felipe (22 ct.), Ovello (21 ct.), Santa Rosa (19 ct.), and Aqua Clara (17 ct.). The special designation and price per pound of the sample marked "Caracas" was not stated. Other South American beans represented were Maracaibo from the northeastern regions of Columbia bordering on Venezuela (22 ct.), Ariba Guayaquil from Ecuador ($16\frac{3}{4}$ ct.), and Bahia, the best known Brazilian grade (13 ct.). Of the West Indian cocoas, Trinidad (15 ct.) was the best, Cuban (13 ct.), St. Domingo ($12\frac{1}{2}$ ct.), Jamaica (11 ct.), and Haiti (10 ct.) being inferior grades. One sample of African cocoa known as San Thomé ($13\frac{1}{2}$ ct.) and one of Ceylon (19 to 21 ct.) complete the list.

The Effects of Roasting on Composition of both the nibs and the shells are shown in the third table. The roasting was carried out under commercial conditions in the factory of a well-known manufacturer, special care being taken that the roasted and unroasted beans accurately represented the same lot. The changes brought about in the shells, although not profound, are greater than in the nibs, theobromine and fiber showing an increase, starch and fat a decrease. Owing doubtless to the protection of the shell the only appreciable changes in the nibs were a slight decrease in theobromine, a distinct decrease in fat, and a distinct increase in fiber. The gain in fiber in both cases is doubtless due to the formation of charcoal, possibly at the expense of fat. The gain in theobromine in the shells and the loss in the nibs suggest a transfer from one to the other by sublimation. The most significant changes were in flavor, which are not brought out by analysis.

Commercial Cocoa and Chocolate.—The fourth table gives summaries of analyses expressed in percentage of air-dry material, also of dry, fat-free material in the case of cocoa, and of dry, sugar-free material in the case of plain and sweet chocolate. The sample of Dutch cocoa (Van Houten), given separately, shows much higher total and water-soluble ash and alkalinity of the ash than the others, which were assumed to have been made without addition of alkali.

Beythien and Pannwitz,¹ who have given special attention to the detection of ground cocoa shells added to cocoa and chocolate, state that the ash content is of little value and the silica and iron content

¹ Z. Unters. Nahr.-Genussm. 1916, **31**, 265.

COMPOSITION OF ROASTED COCOA NIBS (WINTON, SILVERMAN, AND BAILEY)

	Nibs in whole bean	Water	Pro- tein*	Theo- bro- mine	Caf- feine	Fat	Pure starch	Crude starch	Fiber	Other N-free mat- ter	Ash, total	Ash, sol- uble	Sand	Ash, alk.†	Total N	Direct polar- ization ‡	Fat, re- fract. index	Fat, iodine no.	
	%	%	%	%	%	%	%	%	%	%	%	%	%	cc.	%	° V.	° C.	40/n	
	86.1	2.70	11.56	0.95	0.68	51.00	7.81	10.96	2.67	19.22	3.41	1.14	0.07	2.85	2.34	0	33.0	1.4572	33.90
Chuo.....	86.2	3.01	12.56	0.98	0.44	48.20	8.82	12.37	3.20	19.33	3.46	1.27	0.02	2.70	2.44	0	34.0	1.4576	34.2
Venezuelan...	88.6	2.48	12.62	0.92	0.45	48.28	8.65	11.84	3.12	19.92	3.56	1.28	0.06	2.68	2.43	0	32.5	1.4576	34.68
San Felipe....	88.6	2.37	12.75	0.82	0.48	48.11	8.76	11.82	2.57	20.63	3.51	1.10	0.04	2.66	2.43	0	33.5	1.4572	34.84
Ovello.....	87.1	2.80	12.56	0.87	0.38	48.29	8.99	11.82	2.47	20.31	3.33	1.24	0.03	2.80	2.39	0	33.5	1.4576	33.74
Santa Rosa...	88.3	2.65	11.75	1.06	0.56	50.93	8.09	11.46	2.61	19.14	3.21	1.12	0.00	2.65	2.37	0	33.5	1.4572	34.51
Aqua Clara...	86.7	2.72	12.06	0.99	0.55	48.77	8.79	11.73	2.30	20.34	3.48	1.20	0.02	2.80	2.40	0	33.8	1.4574	34.07
Caracas.....	89.6	2.86	11.00	0.84	0.73	50.07	8.76	12.09	2.70	18.89	4.15	1.86	0.00	3.35	2.23	1.6	32.3	1.4576	35.38
Maracaibo....	88.8	2.64	13.06	1.18	0.28	50.39	6.49	9.30	2.21	20.13	3.62	1.17	0.05	1.85	2.54	1.0	34.5	1.4574	34.50
Ariba.....	88.2	2.77	11.19	1.16	0.18	51.39	8.00	11.59	2.23	20.12	2.76	0.73	0.02	1.50	2.20	1.0	33.6	1.4579	36.37
Bahia.....	88.0	3.09	12.37	0.91	0.41	48.28	8.89	12.25	2.70	20.23	3.12	1.39	0.01	2.65	2.38	0	33.5	1.4572	34.19
Trinidad.....	89.3	3.18	11.81	1.10	0.29	52.25	7.19	10.01	2.43	18.64	3.11	1.09	0.00	2.17	2.32	0	33.5	1.4576	35.70
Cuban.....	88.1	2.73	12.37	1.27	0.26	48.44	8.14	10.89	2.51	21.07	3.21	0.97	0.05	2.20	2.45	0.9	32.7	1.4572	33.92
St. Domingo..	91.2	2.29	12.12	1.16	0.22	51.81	6.74	9.46	2.80	19.70	3.16	1.11	0.01	2.25	2.36	1.0	32.3	1.4572	36.17
Jamaica.....	87.2	2.64	12.81	1.06	0.14	51.69	7.08	10.32	2.85	18.60	3.13	0.91	0.04	2.95	2.42	0	35.0	1.4565	35.43
Haiti.....	89.0	2.48	11.19	1.32	0.23	52.24	8.40	11.41	2.81	18.72	2.61	0.90	0.01	1.75	2.27	0.6	33.0	1.4576	57.89
African.....	92.9	2.77	12.19	1.03	0.62	51.60	7.64	10.37	2.79	17.69	3.67	1.23	0.01	2.80	2.45	1.0	32.7	1.4576	35.07
Ceylon.....																			
	86.1	2.29	11.00	0.82	0.14	48.11	6.49	9.30	2.21	17.69	2.61	0.73	0.00	1.50	2.20	0	32.3	1.4565	33.74
Min.....	92.9	3.18	13.06	1.32	0.73	52.25	8.99	12.37	3.20	21.07	4.15	1.86	0.07	3.35	2.54	1.6	35.0	1.4579	37.89
Max.....	88.5	2.72	12.12	1.04	0.40	50.12	8.07	11.16	2.64	19.57	3.32	1.16	0.02	2.51	2.38	0.4	33.3	1.4573	34.97
Aver.....	Dry, fat-free:																		
	0.00	23.37	1.66	0.31	0.00	13.82	19.80	4.70	38.78	5.76	1.60	0.00	3.29	4.74	0
Min.....	0.00	28.05	2.92	1.55	0.00	18.61	25.68	6.56	44.08	8.81	3.96	0.14	7.12	5.41	3.4
Max.....	0.00	25.69	2.21	0.86	0.00	17.10	23.66	5.61	41.49	7.04	2.46	0.05	5.32	5.05	0.9
Aver.....																		

* Total N, less N of theobromine and caffeine, × 6.25. † Cc. N/10 acid per gram of material. ‡ Invert polarization in all cases practically 0.

COMPOSITION OF ROASTED COCOA SHELLS (WINTON, SILVERMAN, AND BAILEY)

	Shells in whole bean	Water	Pro- tein*	Theo- bro- mine	Caf- feine	Fat	Pure starch	Crude starch	Fiber	Other N-free matter	Ash, sol- uble	Sand	Ash, alk.†	Total N	Direct polari- zation	Invert polari- zation
	%	%	%	%	%	%	%	%	%	%	%	%	cc.	%	° V.	° V.
Chuaó.....	13.9	3.71	10.69	0.39	0.15	2.00	3.69	9.87	12.93	45.72	2.52	11.18	5.02	1.87	4.9	
Venezuelan.....	13.8	6.57	17.31	0.46	0.24	1.97	4.44	13.23	16.94	43.83	4.89	0.34	5.92	2.98	6.8	6.4
San Felipe.....	11.4	3.81	12.25	0.61	0.21	2.57	4.17	11.69	14.95	46.13	2.02	5.89	5.60	2.21	4.0	3.2
Ovello.....	11.4	4.14	12.44	0.48	0.17	2.24	3.42	10.23	15.37	45.08	2.82	7.02	5.05	2.19	6.1	
Santa Rosa.....	12.9	4.86	14.94	0.39	0.16	2.95	4.65	11.19	17.31	46.20	4.70	0.84	5.85	2.55	4.0	4.0
Aqua Clara.....	11.7	4.75	13.12	0.42	0.20	3.32	4.65	12.05	15.73	47.21	3.85	3.29	5.37	2.29	6.8	6.4
Caracas.....	13.3	4.52	13.06	0.37	0.15	3.03	4.14	11.07	15.03	48.10	3.94	3.74	5.32	2.25	4.0	4.0
Maracaibo.....	10.4	5.28	16.00	0.46	0.28	3.56	3.36	11.94	15.80	48.03	7.20	0.35	5.73	2.78	6.1	5.6
Ariba.....	11.2	4.47	13.31	0.20	0.10	2.66	4.47	10.89	14.73	51.86	8.20	0.47	5.80	2.22	7.0	6.4
Bahia.....	11.8	4.67	18.06	0.56	0.08	2.22	3.90	10.78	16.90	46.15	7.46	0.05	5.62	3.09	3.1	2.8
Trinidad.....	12.0	5.72	15.31	0.60	0.19	1.98	5.16	13.07	18.35	44.81	7.88	0.20	5.77	2.69	5.2	5.2
Cuban.....	10.7	5.33	2.67	11.91	16.96	7.65	0.88	2.05
St. Domingo.....	11.9	4.48	1.66	10.78	18.47	7.14	0.99	1.76
Jamaica.....	8.8	4.82	2.48	12.46	19.21	11.36	4.30	1.91
Haiti.....	12.8	5.24	5.23	10.80	17.46	16.34	2.49	2.20
African.....	11.0	5.03	18.00	0.90	0.04	2.03	3.60	11.66	18.47	43.71	8.22	0.23	5.22	3.17
Ceylon.....	7.1	5.37	4.57	13.89	18.14	5.07	0.38	1.74
Min.....	8.8	3.71	10.69	0.20	0.04	1.66	3.36	9.87	12.93	43.71	7.14	0.05	5.02	1.74	3.0	2.8
Max.....	13.9	6.57	18.06	0.90	0.28	5.23	5.16	13.89	19.21	51.86	20.72	11.18	5.92	3.17	7.0	6.4
Aver.....	11.5	4.87	14.54	0.49	0.16	2.77	4.14	11.62	16.63	46.40	10.48	2.51	5.52	2.34	5.2	4.9

* Total N, less N of theobromine and caffeine, $\times 6.25$. † Cc. N 10 acid per gram of material.

COMPOSITION OF COCOA NIBS AND SHELLS SHOWING THE EFFECTS OF ROASTING (WINTON, SILVERMAN, AND BAILEY)
(Results on Dry Basis)

	In whole bean	Water (Air-dry material)	Protein*	Theobromine	Caffeine	Fat	Pure starch	Crude starch	Fiber	Other N-free matter	Ash, total	Ash, soluble	Sand	Ash, alk.†	Total N	Direct polarization	Invert polarization	Fat melt. point	Fat refract. index	Fat iodine no.
	%	%	%	%	%	%	%	%	%	%	%	%	%	cc.	%	° V.	° V.	° C.	40 n	
Nibs:																				
Raw.....	85.9	5.13	11.99	1.09	0.44	54.22	7.31	10.68	2.01	19.73	3.21	1.46	0.02	2.48	2.38	0	0	33.0	1.4576	36.33
Under roasted	87.2	4.43	12.36	0.98	0.43	54.08	7.96	10.68	2.16	18.74	3.29	1.44	0.01	2.46	2.41	0	0	32.5	1.4576	35.69
Medium roasted	88.0	3.71	12.01	1.06	0.43	53.63	7.70	10.39	2.82	19.09	3.26	1.51	0.00	2.60	2.38	0	0	32.7	1.4576	35.61
Over roasted...	87.7	3.11	12.26	0.98	0.38	53.15	7.78	10.84	2.93	19.19	3.33	1.47	0.02	2.48	2.38	0	0	32.5	1.4576	35.66
Shells from above:																				
Raw.....	14.1	8.69	13.69	0.36	0.22	4.68	5.03	12.43	14.69	48.85	12.48	3.97	5.03	5.83	2.37	4.3	4.3
Under roasted	12.8	6.94	13.43	0.42	0.26	3.14	4.77	11.24	15.42	49.63	12.93	3.76	4.97	5.80	2.37	5.6	6.0
Medium roasted	12.0	6.01	13.50	0.51	0.22	2.85	4.63	11.03	16.54	48.94	12.81	4.51	4.84	5.69	2.38	5.3	5.1
Over roasted...	12.3	5.16	13.12	0.59	0.25	3.14	4.68	11.92	16.56	48.55	13.11	4.47	5.09	5.64	2.35	6.1	6.3

* Total N, less N of theobromine and caffeine, × 6.25. † Cc. N/10 acid per 1 gram of material.

COMPOSITION OF COMMERCIAL COCOA AND CHOCOLATE (WINTON, SILVERMAN, AND BAILEY)

	Sam- ples	Water	Pro- tein*	Theo- bro- mine	Caf- feine	Fat	Su- crose	Pure starch	Crude starch	Fiber	Other N-free matter	Ash, total	Ash, sol- uble	Sand	Ash, alk.†	Total N	Direct polari- zation	Invert polari- zation
		%	%	%	%	%	%	%	%	%	%	%	%	%	cc.	%	° V.	° V.
Cocoa:	Air-dry:	25																
		7.80	21.44	1.57	0.33	37.22	13.46	18.04	7.81	33.37	8.48	4.62	1.38	3.25	3.80	4.0	0
		5.25	15.81	0.85	0.04	15.79	8.69	13.86	3.22	21.98	3.84	1.76	0.01	1.96	2.81	0	0
	Aver.....	6.24	18.32	1.16	0.16	26.59	11.21	15.89	4.48	26.43	5.39	2.67	0.24	2.45	3.33	0.7	0
	Dry, fat-free:																	
		29.30	2.25	0.49	19.54	27.24	10.44	44.32	11.02	7.34	1.79	4.63	5.31
		24.82	1.41	0.06	11.55	19.59	4.63	36.90	6.70	2.73	0.01	2.91	4.36
	Aver.....	27.32	1.73	0.22	16.73	23.68	6.68	39.31	8.01	3.98	0.34	3.66	4.96
	Cocoa, Dutch Process:	1																
		5.95	18.81	0.94	0.09	28.99	9.35	13.71	4.39	23.50	7.98	6.46	0.19	5.00	3.33	3.0	0
		28.91	1.44	0.14	14.37	21.07	6.75	36.12	12.27	9.93	0.29	7.68	5.11
Chocolate, plain:	Air-dry:	6																
		4.44	12.87	0.87	0.18	53.74	0.00	8.88	12.05	3.17	18.04	3.54	1.67	0.18	2.00	2.37	0	0
		3.24	12.00	0.68	0.09	50.36	0.00	7.47	11.10	2.64	15.27	2.83	1.19	0.02	1.80	2.18	0	0
	Aver.....	3.78	12.36	0.78	0.13	52.19	0.00	8.11	11.63	2.86	16.64	3.15	1.41	0.06	1.93	2.26	0	0
	Dry, sugar-free:																	
		13.39	0.90	0.19	56.22	0.00	9.20	12.48	3.28	18.76	3.68	1.74	0.19	2.08	2.45
		12.55	0.71	0.09	52.38	0.00	7.77	11.55	2.73	15.98	2.90	1.24	0.00	1.88	2.27
	Aver.....	12.85	0.80	0.13	54.25	0.00	8.43	12.09	2.98	17.30	3.26	1.47	0.06	2.01	2.34
	Chocolate, sweet:	12																
		2.71	5.81	0.43	0.14	26.59	63.88	4.02	5.44	1.53	10.79	2.00	0.99	0.13	1.45	1.10	65.6	-20.0
		1.82	3.31	0.30	0.03	19.31	50.60	2.11	3.17	0.72	4.91	0.96	0.55	0.00	0.80	0.65	51.9	-15.7
	Aver.....	2.17	4.58	0.35	0.08	23.51	56.44	2.88	4.16	0.96	7.64	1.40	0.77	0.05	1.08	0.86	58.1	-17.6
Dry, sugar-free:	Air-dry:																	
		12.66	1.00	0.30	67.37	0.00	8.61	11.65	3.28	23.20	4.30	2.24	0.23	3.38	2.36
		8.62	0.70	0.08	52.12	0.00	4.98	8.26	1.74	12.79	2.50	1.43	0.00	1.91	1.69
	Aver.....	11.03	0.84	0.17	56.93	0.00	6.94	10.03	2.31	18.39	3.38	1.87	0.11	2.62	2.08

* Total N, less N of theobromine and caffeine, × 6.25. † Cc. N/10 acid per gram of material.

are of secondary importance since they indicate merely the degree of care taken in handling. They give the following limits of constituents:

	Pro- tein	Pento- sans	Furfu- roids	Fiber	Total ash	Fe ₂ O ₃	Total P ₂ O ₅	Water sol. P ₂ O ₅	Alco- hol sol. P ₂ O ₅	Sol- uble SiO ₂
	%	%	%	%	%	%	%	%	%	%
Nibs:										
Min...	30.3	2.50	0.05	5.69	4.8	0.04	2.48	0.59	0.09	0.02
Max...	35.1	4.60	0.07	8.86	8.8	0.13	2.98	1.08	0.12	0.07
Shells:										
Min...	13.5	7.60	1.10	11.84	6.6	0.14	0.29	trace	0.01	0.08
Max...	17.6	11.20	1.60	21.17	10.6	1.25	1.78	trace	0.05	2.86

Analyses by Lescoq¹ of 12 samples of the nibs from different countries showed: water 4.60 to 7.61, fat 50.1 to 53.56, acidity of the fat as oleic acid 1.28 to 2.64, ash 2.42 to 3.90, and alkalinity of the ash as K₂CO₃ 0.96 to 1.67 per cent. His limits for total ash are in accord with those of Winton, Silverman, and Bailey, but those of Beythien and Pannwitz are much higher.

Germ.—Beythien and Pannwitz² give analyses of 9 samples, as summarized below, and observe that the germ contains less fiber but more theobromine than cocoa. Härtel³ expresses the belief that the samples of Beythien and Pannwitz were contaminated with 15 to 18 per cent of nib tissues and gives his analysis, also here tabulated, of a sample freed with special care from all extraneous matter.

	Water	Pro- tein	Theo- bro- mine	Fat	N-f. ext.	Fiber	Ash, total	Ash, sol.	Sand	PO ₄ total	PO ₄ insol.
	%	%	%	%	%	%	%	%	%	%	%
B. and P.:											
Min.....	5.40	23.52	2.25	13.13	38.08	2.34	5.32	0.01	2.20	0.033
Max.....	8.44	29.26	3.24	17.01	43.45	3.21	7.06	0.22	3.63	0.095
Härtel.....	2.21	32.81*	3.85	2.98	6.76†	4.46†

* Total N × 6.25. † Alkalinity of ash of 100 grams as cc. N acid: total 86.5, soluble 29.5.

¹ Bul. sci. pharmacol. 1923, 30, 341.
² Z. Unters. Nahr.-Genussm. 1923, 46, 223.
³ Ibid. 1924, 47, 264.

Changes During Fermentation.—Lambert¹ has found that the changes taking place during fermentation are brought about chiefly by a yeast (*Saccharomyces theobroma*) and an enzyme, belonging to the oxidases, known as *theobromase*. Brill's experiments² also show that the fermentation is due partly to yeasts and partly to enzymes; in an earlier paper³ he demonstrated that *casease*, *raffinase*, and *oxidase* occur in the fruit pulp and the bean both before and after fermentation, oxidase being especially abundant in the bean, *protease* and *invertase* in the fruit pulp and the fermented bean, and *diastase* only in the fermented bean. Sucrose often disappears entirely, and dextrose at first decreases and then increases slightly. The astringent principles decrease with fermentation, but theobromine shows no regular variation. Perrot⁴ believes the fermentation process unnecessary and recommends soaking the beans in 1 per cent sodium carbonate solution or heating under moderate pressure, removing the pulp mechanically, and slow drying; Knapp,⁵ on the other hand, finds that the Perrot process yields a product having the well-known characters of sun-dried cocoa and inferior to that produced by fermentation.

Analyses of cocoa beans of three types (I Trinidad Calabacillo, II Trinidad Forastero, and III Venezuela Criollo) at different stages of maturity and after fermentation were carried out by McDonald.⁶ In one variety the *tannin* of the beans increased during ripening, in another it decreased, and in the third it showed little difference. Both kernels and shells were rich in tannin, but no correlation with the variety was brought out. *Theobromine* in considerable amount was limited to the beans, the percentage increasing greatly during ripening, but changing little during over-ripening. The content varied little with the type. The maximum *fat* content was reached at full maturity, being slightly higher in type II than in the others. Fermentation caused an increase in *tannin* and *fat* content and a decrease in *theobromine* content in the kernel with corresponding increase in the shell.

Milk Chocolate.—Three leading brands of milk chocolate, as analyzed by Dubois,⁷ contained sucrose 40.90 to 46.78, aver. **44.47**, and lactose 8.24 to 9.12, aver. **8.53** per cent. Reichert-Meissl numbers of

¹ Bul. sci. pharmacol. 1912, **18**, 574.

² Philippine J. Sci. 1917, **12A**, 1.

³ Ibid. 1915, **10**, 123.

⁴ Compt. rend. 1913, **156**, 1394.

⁵ J. Soc. Chem. Ind. 1916, **35**, 136.

⁶ Imp. Col. Trop. Agr. Trinidad, 1936, 6th Ann. Rep. Cacao Res. pp. 34, 40, 43.

⁷ J. Am. Chem. Soc. 1907, **29**, 556.

the fat were 5.3 to 5.8, aver. **5.5**, indicating 22.1 to 24.2, aver. **23.1** per cent of butter fat in the total fat.

The following is a summary of analyses of milk chocolate by Booth: ¹

COMPOSITION OF MILK CHOCOLATE (BOOTH)

	Samples	Protein (N×6.25)	Milk fat	Cocoa butter	Lactose	Sucrose
		%	%	%	%	%
English:	10					
Min.	4.8*	2.6	21.0	3.8	32.4
Max.	10.5*	8.3	31.6	11.1	54.3
Aver.	7.4*	5.5	26.3	8.0	43.2
Continental:	10					
Min.	6.9*	5.7	15.6	5.2	35.0
Max.	8.1*	13.6	27.7	11.0	52.7
Aver.	7.7*	8.1	22.7	8.2	42.6

* 3 samples.

The complete analysis of milk chocolate presents certain difficulties on account of the complex mixture of proteins, fats, and carbohydrates; hence whenever possible the composition should be obtained by calculation from the amounts and analyses of the chocolate, sugar, and milk powder used in the mixture.

Compounds of Chocolate and Cocoa with numerous other foods and food flavors have appeared from time to time on the market, some being designed as concentrated foods for soldiers or explorers, others merely as confections. Included in the list of added substances are various cereals and cereal preparations, including maize starch, peas, shelled peanuts, almonds, hazelnuts, other nuts, potato flour, acorn meats, sago, arrowroot, gum arabic, Iceland moss, dried eggs, dried meat and meat extracts, peptones, milk powder, casein, vanilla, vanillin, coumarin, spices, inorganic salts, saccharine, raisins, and xanti currants.

CONSTITUENTS. Proteins.—Little attention has been paid to the nitrogenous constituents other than alkaloids. The following results by Stutzer ² on 4 brands of cocoa show the amounts of nitrogenous constituents in pure cocoa and cocoa treated with chemicals:

¹ Analyst 1909, **34**, 139.

² Z. angew. Chem. 1891, **4**, 368.

	Theobro- mine	Am- monia	Amides	Digest- ible protein	Indigest- ible protein	Total nitro- genous matter	Ash
	%	%	%	%	%	%	%
Pure cocoa	1.92	0.06	1.43	10.25	7.18	20.84	5.05
Dutch process	1.73	0.03	1.25	7.68	9.19	19.88	8.30
Ammonia process (?)							
I	1.98	0.46	0.31	10.50	7.68	20.93	5.18
II	1.80	0.33	1.31	7.81	8.00	19.25	5.43

Purine Bases. *Caffeine*.—See Introduction to Part II.

Theobromine.—See Introduction to Part II.

Wadsworth,¹ by his method for the determination of theobromine, reports 0.9 to 1.7 per cent in the air-dry and 2.2 to 3.9 per cent in the dry, fat-free nibs. These figures are higher than those given by other authors. In the germ he found 2.10 per cent of theobromine. He states there is a loss of the alkaloid during fermentation but not during roasting.

Figures reported by Kreutz,² on 6 of the leading brands of cocoa, show a range in total theobromine of 1.99 to 3.85 per cent, of which less than one-third to over one-half was free, the remainder being combined as glucoside.

Other Nitrogenous Compounds. *Choline*, $C_5H_{15}NO_2$.—Results by Nottbohm and Mayer³ on choline in cocoa beans range from 0.102 to 0.149 per cent, about half of which was soluble in hot alcohol and only a trace in ether.

Fat.—Cocoa butter, the commercial name for cocoa fat, is characterized by its high melting point. It is obtained in the manufacture of cocoa and is often added to give firmness to the chocolate used for coating confectionery.

Physical and Chemical Values.—The results of Winton, Silverman, and Bailey on melting point, refractive index, and iodine number of the ether extract of cocoa nibs are summarized in a foregoing table. Compared with their results the minimum melting point (28° C.) given by Lewkowitsch⁴ is lower and the maximum iodine number

¹ Analyst 1921, 46, 32; 1922, 47, 152.

² Z. Unters. Nahr.-Genussm. 1908, 16, 579.

³ Z. Unters. Lebensm. 1933, 65, 55.

⁴ Chem. Technol. Anal. Oils, etc., London, 1914, 2, 589.

(41.7) is nearly 4 points higher. Allen¹ gives 0.860 as the specific gravity at 100° C. of cocoa butter. The saponification number, as found by several authors, ranges from 192 to 202. Grossfeld, Mechlinski, Seith, and Schnetka² found no difference in the saponification number and the percentage of unsaponifiable matter in expressed cocoa butter and the ether extract of chocolate.

In the samples of pure commercial chocolate, both plain and sweet, and cocoa, examined by Winton, Silverman, and Bailey, the values of the ether extract differed slightly from those of the ether extract of the nibs, probably owing to changes during grinding and storage.

	Samples	Melting point °C.	Ref. Ind. 40° C.	Iodine No.
Plain chocolate:	6			
Min.	29.5	1.4570	35.3
Max.	31.5	1.4576	36.5
Aver.	30.4	1.4572	35.9
Sweet chocolate:	12			
Min.	28.5	1.4567	32.9
Max.	31.0	1.4574	39.6
Aver.	30.3	1.4572	35.6

The ether extract of chocolate and cocoa containing added flour or starch, examined by the same authors, differed little in its values from that of cocoa nibs, but the ether extract of the coating removed from chocolate confectionery³ showed much wider ranges in values—refractive index at 40° C. 1.4555 to 1.4591, saponification number 183.2 to 208.7, iodine number 27.6 to 54.4—pointing clearly to foreign fat.

Beythein and Pannwitz⁴ and Härtel⁴ give the following values of germ fat: refractive index at 40° C. 1.4573 to 1.4579, 1.4675; saponification number —, 169.8; iodine number 40.39 to 42.57, 68.8; Reichert-Meissl number 0.40 to 0.84, —; Polenske number 0.10 to 0.40, —.

Vizern and Guillot⁵ in the fat (2.93 per cent) of cacao shells, obtained by petroleum ether extraction, found the following values:

¹ Com'l. Org. Anal., Philadelphia, 1912, 6, 701.

² Z. Unters. Lebensm. 1931, 62, 441.

³ Connecticut Agr. Exp. Sta. Rep. 1906, p. 136.

⁴ Loc. cit.

⁵ Ann. fals. 1936, 29, 484.

melting point 34° C., iodine number 57, and unsaponifiable matter 8.80 per cent.

Composition.—The presence of glycerides of arachidic acid, reported by earlier authors,¹ needs confirmation. The existence of theobromic acid, claimed by Kingzett,² has been disproved by the author himself³ as well as others, but he states there is evidence pointing to lauric acid.

The extensive studies of Lea⁴ led to the following conclusions as to the percentage composition:

	%
Saturated glycerides (mostly mixed palmitic stearins).....	2.5
Mono-oleo-disaturated glycerides:	
Oleodistearins.....	10%
Oleopalmitostearins, at least.....	50-60%
Total.....	77.0
Dioleo-monosaturated glycerides (mostly dioleostearins).....	16.0
Triolein, possibly.....	4.0
	<hr/> 99.5

Bougault and Schuster,⁵ by oxidizing cocoa butter by Hilditch's method, which affects only the double bond, obtained an amount of palmitostearoazelein, a new triglyceride, that indicated the presence of about 36 per cent of *palmitostearoölein* in the fat. By further treatment they prepared a new diglyceride, palmitostearin. Hilditch and Saletore⁶ claim that the latter was probably ethyl stearate formed from part of the combined stearic acid, but, after repetition of their work, Bougault and Schuster⁷ adhered to their previous conclusion.

Hilditch and Stainsby⁸ calculated from data obtained on the whole fats and the fully saturated glycerides after partial and complete hydrogenation not only the content of the individual fatty acids in the total fatty acids (oleic 40, stearic 34, palmitic 26) but also the content of mixed glycerides in the total glycerides. Their results, which follow, in the main agree closely with those of Lea.

¹ Graf: Arch Pharm. 1888, **26**, 830; Benedikt and Hazura: Monatsh. Chem. 1889, **10**, 353.

² J. Chem. Soc. 1878, **33**, 38.

³ Chem. Trade J. 1922, **71**, 699.

⁴ J. Soc. Chem. Ind. 1929, **48**, 41.

⁵ Compt. rend. 1931, **192**, 953; J. pharm. chim. 1931, **14**, 145.

⁶ J. Soc. Chem. Ind. 1933, **52**, 101T.

⁷ Bul. soc. chim. 1934, [5], **1**, 1416.

⁸ J. Soc. Chem. Ind. 1936, **55**, 95T.

Oleopalmitostearins.....	52
Oleodistearins.....	19
Stearodioleins.....	12
Palmitodioleins.....	9
Oleodipalmitins.....	6
Palmitostearins.....	2
	<hr/>
	100

Kaufmann,¹ by absorption spectra methods, was unable to distinguish pressed from extracted cocoa butter. From the iodine number (34.9 to 37.6) and the thiocyanogen number (32.7 to 34.9), he² calculated that 34.2 to 37.3 per cent of *oleic glycerides* and 2.4 to 4.3 per cent of *linolic glycerides* were present. Previously the existence of linolic acid in this fat was in dispute. Godbole and Sadgopal³ obtained the following figures for cocoa butter, calculated from the iodine and thiocyanogen numbers: oleic acid 38.14, linolic acid 0.66 per cent.

Unsaponifiable Matter.—Commercial cocoa butter contains about 1 per cent of unsaponifiable matter. No data on the kind and amount of sterols are available, but Acheenich⁴ reports in 2 samples of cocoa shells 125, in 12 samples 31 to 63, and in cocoa butter 1 international unit of vitamin D per gram, and slightly decreased amounts after roasting.

Cocoa Butter Substitutes.—Elsson⁵ recommends as a *substitute for cacao butter* 96 parts of "Butyrol," a hydrogenated fat melting at 35.5° C., mixed with 2 parts of anhydrous lanolin melting at 38 to 39° C. and 2 parts of yellow wax.

Vizern and Guillot⁶ endorse the Halphen test for detection of illipé (5 per cent) and karite (20 per cent) butter in cacao butter, but recommend that the time of standing after bromination and dilution with petroleum ether be reduced from 12 hours to 15 minutes. They do not consider that the procedure proposed by Colombier and Chaize⁷ has any advantage over the original Halphen method.

Volatile Oil.—Müller⁸ claims that the salutary and aromatic constituents reside in the fat-free portion of the cotyledons, but it is not clear in what specific group he places them.

¹ Chem. Umschau Fette, Oele, Wachse, Harze 1931, **38**, 241.

² Z. angew. Chem. 1929, **42**, 402.

³ Allgem. Oel- Fett-Ztg. 1934, **31**, 435.

⁴ Biedermanns Zentr. B. Tierernähr. 1936, **8**, 276.

⁵ Sovet. Farm. 1934, **5**, No. 12, 26.

⁶ Loc. cit.

⁷ Ann. fals. 1928, **21**, 91.

⁸ Chem. Ztg. 1908, **53**, 57.

Bainbridge and Davies¹ found the volatile oil to be the source of the flavor and aroma. By distillation they secured a yield of 1.2 per cent of volatile oil with a strong chocolate odor and flavor, more than half of which on fractioning was found to be *d-linalol*, the remainder consisting of *esters*, also *octoic*, *hexoic*, and *n-nonoic acids* of the fatty acid group.

Fincke² separates the flavoring constituents of the cocoa bean into three groups: (1) readily volatile and partly undesirable substances; (2) fat-soluble, difficultly volatile, but highly aromatic substances; and (3) tannin-like compounds.

Organic Acids. *Oxalic Acid*.—Girard³ found in raw cocoa nibs and shells respectively 0.158 and 0.189 per cent of oxalic acid in the form of alkali-oxalate and 0.152 and 0.084 per cent in the form of calcium oxalate. The amounts were not appreciably changed by roasting. It therefore appears that the cocoa bean belongs in the same class as spinach, rhubarb, and sorrel as regards this constituent. Albahary⁴ found that in ordinary cocoa 0.016 per cent of oxalic acid was in the form of alkaline salts and 0.376 per cent in the form of calcium oxalate, while in the Dutch process cocoa 0.365 per cent was in the form of alkaline salts and only 0.019 per cent in the form of calcium oxalate. It is thus evident that although the results for total oxalic acid by these two authors agree substantially they disagree widely as to the amounts in the two forms. Arbenz⁵ reports 0.48 per cent of oxalic acid in cocoa. Grossfeld and Lindemann⁶ obtained an increased yield of oxalic acid on long heating of the calcium precipitate from a hydrochloric acid solution which they believe was due to substances hydrolyzing to oxalic acid present in the bean and the shell. Widmark and Ahldin⁷ found in cocoa 0.65 per cent of oxalic acid, which is nearly twice that reported by Esbach⁸ (0.35).

Acetic Acid, if formed during fermentation, is largely driven off during roasting.

Fincke and Niemeyer⁹ detected free acetic acid in the kernels, the shell, and the air between the sacks of cocoa beans. The volatile acid

¹ J. Chem. Soc. 1912, **101**, 2209.

² Kazett 1932, **21**, 381.

³ Rev. soc. hyg. aliment. 1909, **7**, 83.

⁴ 7th Int. Cong. App. Chem. 1909, **8c**, 175.

⁵ Mitt. Lebensm. Hyg. 1917, **8**, 98.

⁶ Z. Unters. Lebensm. 1934, **68**, 612.

⁷ Biochem. Z. 1933, **265**, 241.

⁸ Bul. gén. therap. méd. chir. obstet. 1883, **104**, 407.

⁹ Z. Unters. Lebensm. 1937, **74**, 387.

of the beans is largely acetic. Ether extracts more of the acid than petroleum ether; the acid number of the extracted fat, however, is not due to acetic acid.

Tartaric Acid.—Boussingault,¹ Weigmann,² and other authors have reported tartaric acid in cocoa beans, but in view of the conflicting evidence as to the nature of the organic acids in fruits their findings need confirmation by modern methods.

Citric Acid.—Hartmann and Hillig³ found 0.53 per cent, free and combined, in cocoa.

Pectic Acid.—In 2 samples of cocoa shells Winkler⁴ found 3.5 to 3.89 per cent of pectic acid. In chocolate liquors, a content over 0.4 per cent is suspicious.

Carbohydrates. *Starch*.—See analyses in tables above.

Pentosans.—Lühlig and Segin,⁵ in dry fat-free cocoa nibs, report 2.51 to 4.58 per cent of pentosans and in dry cocoa shells 7.59 to 11.23 per cent. Adan's results⁶ fall within the same limits.

Maurenbrecher and Tollens⁷ isolated, after acid hydrolysis of both powdered nibs and shells, *l*-arabinose, *d*-galactose, and *d*-glucose and obtained evidence of the probable presence of *xylose*.

Cellulose and Lignin.—These, as shown by the fiber content and microchemical tests, are particularly abundant in the shells. Thaler⁸ demonstrated that the composition of the "skeletal" (cell wall) substance of the nibs (kernels), obtained by treatment with chlorine oxide, is practically the same as that of the shell and is similar to that of beechwood. The following results were obtained on the shells and kernels respectively: *cellulose* 28.15 and 9.10, *xylan* 4.94 and 1.58, *acetyl* (COCH₂) 1.43 and 0.36 and *total skeletal matter* 34.52 and 11.04 per cent. The percentage of cellulose in both parts is markedly greater than that of *crude fiber*.

Colors.—*Cocoa-Red*, although the subject of a number of investigations, is of uncertain composition. It was formerly thought that it does not exist in the bean fresh from the tree, but is formed during fermentation or curing. The work done prior to 1892 is reviewed by

¹ Ann. chim. phys. 1883, [5], 28, 433.

² König: Chem. mensch. Nahr.-Genussm., Berlin, 1903, 1, 1021.

³ J. Ass. Off. Agr. Chem. 1934, 17, 522.

⁴ Ibid. 1937, 20, 415.

⁵ Z. Unters. Nahr.-Genussm. 1906, 12, 161.

⁶ 7th Int. Cong. App. Chem. 1909, 8c, 203, 204.

⁷ Ber. 1906, 39, 3576.

⁸ Z. Unters. Lebensm. 1937, 73, 121, 129.

Ewell,¹ who states: "The coloring matter of the bean seems to be related to the tannins, but authorities differ as to whether it is a decomposition product of a tannin, or whether a tannin is the result of its decomposition." Hassall² notes that cocoa-red is obtained by precipitation of an aqueous or alcoholic decoction with lead acetate and decomposition of the washed precipitate with hydrogen sulphide, also that its solution gives a green or brown precipitate with ferric salts and a green or violet precipitate with ferrous salts. He further states that on oxidation of cocoa-red a tannic acid precipitable by gelatin is formed. Blyth,³ in his analytical method, utilizes the lead acetate and hydrogen sulphide reactions, while Ulrich,⁴ in his method, which has been investigated by Lythgoe,⁵ precipitates with ferrous chloride.

Hilger⁶ extracted cocoa beans successively with petroleum ether and water, thus removing fat, theobromine, caffeine, soluble carbohydrates, and mineral matter. He then extracted the residue with alcohol and from the solution obtained what he considered to be pure cocoa-red, a substance related to ordinary tannin, to which he assigned the formula $C_{17}H_{12}(OH)_{10}$. Both his and Schweitzer's experiments⁷ indicate that cocoa-red, together with theobromine, caffeine, and dextrose, is formed by the action of an amylase on a glucoside, *cacaonin*. Schweitzer considers that the glucoside consists of 1 part each of cocoa-red and theobromine and 6 parts of dextrose.

More recent studies by Fincke⁸ show that the pigment cocoa-red is present in the fresh bean but during fermentation, roasting, and grinding another pigment, *cocoa-brown*, is gradually formed, partly from cocoa-red and partly from a parent substance common to both. It is cocoa-brown that gives cocoa products their characteristic color. Cocoa-red is soluble in alcohol. In acid solution it is bright red, in alkaline solution green or green-blue, and in neutral solution violet. Cocoa-brown is only slightly soluble in alcohol but readily soluble in water containing alkali.

Steinmann⁹ differentiates in Java cacao two colors, both formed in the light from a colorless mother substance: (1) cocoa-red, easily

¹ U. S. Dept. Agr., Div. Chem. 1892, Bul. **13**, 940.

² Food: Its Adulteration, etc., London, 1876, p. 194.

³ Foods, etc., London, 1909, p. 369.

⁴ Arch. Pharm. 1911, **249**, 524.

⁵ J. Ass. Off. Agr. Chem. 1916, **1**, 550.

⁶ Apoth. Ztg. 1892, **7**, 469.

⁷ Pharm. Ztg. 1898, **43**, 389.

⁸ Z. Unters. Lebensm. 1928, **55**, 559.

⁹ Ibid. 1933, **65**, 454.

soluble in alcohol, and (2) cocoa-brown, difficultly soluble in alcohol but soluble in alkaline solutions, the latter changing to the former on treatment with acid. Colorless unfermented beans contain neither substance. Cocoa-red exists in the bean partly bound, partly free. The free cocoa-red of unfermented violet beans formed in the light disappears during fermentation, but is re-formed from the combined color by acetic and other acids which appear during prolonged fermentation.

Phosphorus-Organic Compounds.—Rewald and Christlieb,¹ by means of a mixture of benzene and alcohol, extracted 0.02 to 0.27, aver. **0.10** per cent of phosphatide calculated as lecithin with 3.94 per cent of phosphorus.

Lecithin.—The results of Nottbohm and Mayer² indicate that free lecithin is absent, although other phosphatides may be present in the alcohol extract.

The alcohol-soluble phosphatide content of 6 brands of pure cocoa examined by Braunsdorf³ ranged from 0.389 to 0.980 per cent calculated as lecithin ($P_2O_5 \times 11.32$) in the fat-free, dry substance. The ether-soluble phosphatides ranged from 0.053 to 0.55 per cent, calculated to 100 grams of fat, corresponding to 0.9 to 8.5 mg. per 100 grams in the cocoa. The ratio of alcohol-soluble to total phosphoric acid ranged from 1 : 27.4 to 1 : 63.6. Because of these wide variations, attempts to detect added lecithin seem futile.

Mineral Constituents.—The results of Bordas⁴ on the ash of the nibs of 10 varieties of cocoa beans and of single analyses of cocoa germs and shells, also of Beytheim and Pannwitz⁵ and Härtel⁵ on the ash of the germ are summarized on the next page.

Grossfeld and Lindemann⁶ gives figures for CaO, MgO, and P_2O_5 in accord with the average of Bordas's analyses, but show about three times as much chlorine.

Minor Mineral Constituents. *Iron.*—Beans, peeled 24 mg. per kilo, as sold (Bunge).⁷ Bitter chocolate 31.5 and cocoa 31.3 mg. per kilo, fresh basis (Peterson and Elvehjem).⁸ Beans, peeled 33.3 to 35.5, aver. **34.3**; shells 228.6 to 571.0,

¹ Chem. Ztg. 1931, **55**, 393.

² Z. Unters. Lebensm. 1933, **65**, 55.

³ Ibid. 1937, **73**, 38.

⁴ 7th Int. Cong. App. Chem. 1909, **8c**, 188.

⁵ Loc. cit.

⁶ Z. Unters. Lebensm. 1935, **69**, 45.

⁷ Sherman: U. S. Dept. Agr., Off. Exp. Sta. 1907, Bul. **185**.

⁸ J. Biol. Chem. 1928, **78**, 215.

COMPOSITION OF ASH OF COCOA NIBS, GERMS, AND SHELLS

	Ash, total	Ash, sol.	Ash, insol.	K ₂ O	Na ₂ O	CaO	MgO	Fe ₂ O ₃ *	P ₂ O ₅	SO ₃	SiO ₂ †	Cl	CO ₂
	%	%	%	%	%	%	%	%	%	%	%	%	%
<i>Nibs</i>													
Bordas:													
Min.	2.60	27.4	65.9	30.4	0.2	3.4	13.0	0.2	25.6	2.6	0.5	0.2	2.8
Max.	3.84	34.1	72.6	38.5	2.6	5.3	17.7	1.9	33.8	4.0	7.3	0.5	9.2
Aver.	3.41	31.9	68.1	34.9	1.4	4.2	15.5	0.9	30.5	3.2	3.4	0.3	5.7
<i>Germs</i>													
Bordas	56.7	43.3	54.5	0.0	4.3	9.8	0.4	18.5	4.3	1.0	0.5	4.9
B. and P													
Min.	5.32	29.81	0.52	3.02	10.52	...	27.43	4.17	0.18
Max.	7.06	37.02	4.12	5.16	15.44	...	35.34	6.96	0.42
Härtel	6.76	37.02	5.21	13.08	...	24.07	5.21
<i>Shells</i>													
Bordas	43.2	56.8	41.5	3.5	4.7	7.4	3.6	8.5	2.5	19.1	0.8	94.

* Includes Al₂O₃. † Includes sand.

aver. **359.0**; cocoa, as purchased (6 samples) 80 to 190, aver. **126.4** mg. per kilo (Toscani and Reznikoff).¹

Manganese.—Bitter chocolate 32.2 and cocoa 37.0 mg. per kilo, dry basis (Peterson and Skinner).²

Copper.—Bahia: nibs 34, shells 35; Caracas: nibs 20, shells 40; Guayaquil: nibs 27, shells 14 mg. per kilo (Formenti).³ Bitter chocolate 26.7 and cocoa 33.4 mg. per kilo, fresh basis (Lindow, Elvehjem, and Peterson).⁴

Boron.—Cocoa beans and cocoa 0.02 to 0.08 per cent of H₃BO₃ (Dodd).⁵

¹ J. Nutrition 1934, **7**, 79.

² Ibid. 1931, **4**, 419.

³ Z. Unters. Nahr.-Genussm. 1913, **25**, 149.

⁴ J. Biol. Chem. 1929, **82**, 465.

⁵ Analyst 1927, **52**, 459.

COLA NUT

Cola spp.

Fr. Noix de Kola. Ger. Kolanuss.

Formerly the large cola nut with two cotyledons was considered to be the seed of *C. acuminata* R. Br., but more recently the large nut has been attributed to *C. vera* K. Schum. (*C. nitida* A. Chev.) and the small nut with four cotyledons to *C. acuminata* (P. Beauv.) Schott et Endl. and other species.¹ The nuts which enter the world commerce are largely those with two cotyledons, although mixing with small cola nuts, according to Schumann, is practiced. Tschirch and Oesterle,² however, basing their belief on the examinations of specimens from the Buitenzorg Botanic Garden, hold to the view that seeds of *C. acuminata* P. Beauv. have two cotyledons and therefore pass as large cola nuts. There is much confusion in the nomenclature.

The species are indigenous to tropical and subtropical Africa, where the natives chew the nuts for their stimulating action. The nuts are also said to be used in the preparation of effervescent caffeine-containing beverages in the United States, although cheaper sources of caffeine are there available. Outside of Africa they are chiefly known as a drug.

MACROSCOPIC STRUCTURE.—Only the dried *cotyledons* with traces of the spermoderm are present in the commercial product. In size and shape these resemble the cotyledons of the Spanish chestnut, but are of a reddish brown color.

MICROSCOPIC STRUCTURE.—Hanausek³ was among the first to describe the histological elements of the large cola nut which he assumed was from *C. acuminata* Schott et Endl. Several later authors have accepted his findings.

Starch grains are the most abundant cell contents. The larger grains, according to Hanausek, range from 16 to 28 μ in diameter and are mostly globular, ovate, or kidney-shaped. His observation that

¹ Hartwich: Handb. Nahrungsm.-Unters., Leipzig, 1915, 2, 358.

² Anat. Atlas, Leipzig, 1900, p. 347.

³ Z. oesterr. Apoth. Ver. 1877, 15, 534.

numerous rifts occur at the hilum is confirmed by other writers, but his statement that the hilum is central applies only to some of the more regularly formed grains, since both Tschirch and Oesterle¹ and Hartwich² show that the hilum is usually eccentric and located in the broad end of oval or pear-shaped grains. In one sample of large cola nuts Hartwich found starch grains up to 46 μ long.

CHEMICAL COMPOSITION.—The early analyses of Attfield³ and Heckel and Schlagdenhauffen⁴ show high percentages of fiber, indicating that the shell (spermoderm) had not been removed. They are nevertheless instructive and are here reproduced together with a summary of analyses of 12 samples by Uffelmann and Bömer:⁵

COMPOSITION OF COLA NUT

	Water	Pro- tein*	Caf- feine	Theo- bromine	Fat	Sugar	Gum	Starch	Fiber	Tan- nin	Ash
	%	%	%	%	%	%	%	%	%	%	%
Attfield.....	13.65	6.33	2.13	1.52	10.67		42.50	20.00†	3.20
H. and S.....	11.91	6.76	2.35	0.02	0.59	2.88	3.04	33.75	29.83‡	1.62§	3.40
U. and B.:											
Min.....	8.43	7.38	1.71	0.88	35.30	5.23	2.13	2.43
Max.....	15.54	10.69	2.77	2.15	50.27	12.27	4.88	3.28
Aver.....	13.35	9.56	2.08	1.35	45.44	7.01	3.79	2.90

* Total N \times 6.25. † Includes "color." ‡ By difference. § Color 2.56%.

According to Vargas,⁶ fresh cultivated cola nut, with 40 per cent of water, contains caffeine 1.41, theobromine traces, and mineral salts 1.96 per cent.

Purine Bases.—Both *caffeine* and *theobromine* appear to be present although the amount of the latter is small, reaching 0.10 per cent in no analysis that has come to our notice.

Knox and Prescott⁷ report the following range in 5 samples: free caffeine 1.12 to 1.84, combined caffeine 1.62 to 2.09, and total caffeine 2.75 to 3.65 per cent.

The alkaloids are believed to be combined with tannin and glucose as *glucosides* which are split up by enzymes present in the bean.

¹ Loc. cit.

² Handbuch Nahrungsm. Unters., Leipzig, 1915, 2, 360.

³ Pharm. J. 1864-5 [2], 6, 457.

⁴ J. pharm. chim. 1883, 7, 556; 1885, 8, 81, 177, 289.

⁵ Z. angew. Chem. 1894, 7, 710.

⁶ Bol. ass. brasil. pharm. 1934, 15, 250.

⁷ J. Am. Chem. Soc. 1897, 19, 63.

SEEDS OF THE MADDER FAMILY

(*Rubiaceæ*)

SEEDS of common or Arabian coffee (*Coffea arabica* L.) and several other species of the same genus are the only foods of this family recognized in world commerce, although several delicious fruits, notably of *Vangueria madagascariensis* Gmel which has been introduced into Florida, are of local importance. Other economic plants of the family yield well-known drugs (e.g., cinchona bark, ipecac) and dyestuffs (e.g., madder, gambier). Species of *Galium* known as bedstraws (Vol. I) are common weeds which like coffee have reserve material in the cell wall of the endosperm.

Group Characters.—The outstanding characteristics of the genus *Coffea* are reserve carbohydrate in the knotty thickened cell walls and caffeine in the cell contents of the endosperm.

Caffeine, however, is not present in some species. Bertrand¹ found none in the seeds of the four species growing in Madagascar named below. Hartwich² confirms his conclusion and extends it to include *C. bengalensis*, but cautions against generalities since in some cases only a single bean was available for tests. In the seeds of *C. mauritiana* Bertrand found only 0.07 per cent. The caffeine issue as well as others is beclouded by the uncertain status of certain alleged species.

Economic Species.—Hartwich² describes the gross and minute characters of the beans of the following "species" which are of more or less importance in their native countries and according to Cramer³ have been introduced on an experimental or commercial scale into Java:

Liberian coffee (*C. liberica* Hiern.). Berries larger than of common coffee. Hybrids of the two species are cultivated. Tropical West Africa.

¹ Compt. rend. 1905, **141**, 209.

² Z. Unters. Nahr.-Genussm. 1909, **18**, 723; Handb. Nahrungsm. Unters. Leipzig, 1915, **2**, 309.

³ Meded. Dept. Landb. 1913, Nr. 11.

Café marron (*C. mauritiana* Lam.). Berries long, narrowed at end, of bitter taste. Mascarene Islands.

Congo coffee (*C. canephora* Pierre) and its variety Quillu coffee. French Equatorial Africa.

Robusta coffee (*C. robusta* Chev.). According to De Wildeman a variety of *C. canephora* Pierre. French and Belgian Congo.

Zanzibar coffee (*C. Zanguebariæ* Lour.). East Africa.

Bengal coffee (*C. bengalensis* Roxb.). Berries inferior. India, Indo-China, and East Indies.

Sierra Leone coffee (*C. stenophylla* Don). Exploited by English experts. Berries excellent. West Africa.

Abeocuta coffee (*C. Abeocutæ*). Possibly a variety of *C. liberica*. Nigeria.

Uganda coffee (*C. ugandæ*). Related to *C. canephora* and *C. robusta*. East Africa.

Snoussi coffee (*C. excelsa* Chev.). Chad territory, Central Africa.

Bertrand¹ has assigned the following specific names to four trees found in Madagascar: *C. Humboltiana*, *C. Gallienii*, *C. Bonnieri*, *C. Mogeneti*.

Tests made by Pritzker and Jungkunz² for caffeine in the roasted beans of the wild species *C. perrieri* and *C. dubardi* gave negative results.

. COFFEE

Coffea arabica L.

Fr. Café. Sp. Café. It. Caffè. Ger. Kaffee.

Although the infusion is valuable chiefly for its flavoring and stimulating principles and contains only a small amount of nutritive constituents, many families spend more for coffee than for bread. Because of the high cost, as well as the adulteration to which it has been subject, much has been written on the microscopy, chemistry, and analysis of coffee.

The species is a native of Abyssinia and neighboring regions in Africa where the berries have been gathered from time immemorial, although probably only in recent centuries from cultivated trees. The cultivation of the tree spread first to Arabia, and coffee drinking was taken up by Mohammedan nations. It was not until about 1700

¹ Loc. cit.

² Z. Unters. Lebensm. 1938, 75, 34.

that the tree was introduced by the Dutch into Java and Surinam and still later throughout the East and West Indies and South America.

At the present time the finest grades are Arabian or short berry Mocha, produced in the province of Yemen and shipped from the port of Aden, and Abyssinian or long berry Mocha. The total production of Mocha, however, is small. Brazil leads the world in coffee growing, the shipments being made chiefly from Rio de Janeiro (Rio coffee) and São Paulo (Santos coffee). Other coffee regions in the Western Hemisphere are Colombia (Bogota), Venezuela (Maracaibo), Guiana, Ecuador, Puerto Rico, Santo Domingo, Haiti, Jamaica, and other West Indian islands, Mexico, and Central America, and in the Eastern Hemisphere Java, Sumatra, and other islands of the East Indies, India, Ceylon, and East and West Africa.

Decortication.—The primitive *dry process*, still followed in the Near East, consists in merely sun drying the berries, crushing them between rollers, and separating the beans from the outer coats. The modern or *wet process* consists first in running the fresh berries through the pulper and removing the greater part of the fleshy tissues by mechanical means. The remainder of the pulp is removed from the endocarp by fermentation and washing, after which the beans, still enclosed in the parchmentlike endocarp and the silver skin or spermoderm, are dried either in the sun or with the aid of artificial heat. Finally the beans are put through shelling and polishing machines.

Roasting develops the aroma and changes the composition in other respects. It is carried out by the importer or wholesaler in special machinery requiring careful adjustment of the temperatures.

Grinding is also often performed on a large scale, in which case the ground product is stored in tight metal or paraffined containers to prevent deterioration. Many, however, still prefer to have the beans freshly ground by the grocer or in the kitchen.

Preparation of Beverage.—The Turkish method is carried out without removal of the grounds, the bean previously having been reduced to a fine powder, hence all constituents of the bean are acted on by the digestive juices and, so it is claimed, the beverage is less injurious than that made with removal of the grounds.

Occidental methods, whether involving direct boiling and decantation or percolation with boiling water, remove only about 25 per cent of solid matter from the coffee, the remainder being lost in the grounds.

Much has been written on the respective merits of boiling and per-

colating, numerous devices having been patented for the operations, simple though they may appear.

Caffeine-free Coffee.—Several processes have been patented for the removal of caffeine from coffee on the assumption that this is the injurious constituent. The earlier processes removed desirable principles or did not remove all the caffeine. One process depends on extraction with water, removal of caffeine from this extract, and return of the residue to the coffee. The brands now most extensively sold in the United States are Kaffee Hag, Sanka, and Dekofa, which as noted below are practically free from caffeine.

Tannin-free Coffee.—At one time coffee from which the chaff had been removed was falsely claimed to contain less tannin and caffeine than whole coffee. The removal of the substances classed together as caffetannic acid seems impracticable. Analyses are given under Chemical Composition.

Vacuum-Packed Coffee is advocated by some as a hygienic coffee as noted under Chemical Composition.

Coffee Extracts, usually in a semi-solid or pasty condition, have been placed on the market for the use of soldiers, campers, and others demanding compactness and ease of preparation of the beverage. The product is packed in jars, collapsible tubes, and other convenient containers. Evaporated milk or milk powder and sugar are sometimes mixed with the extract in proper proportion. During the World War large quantities of coffee extracts of this nature were used by the soldiers.

Chicory in some sections, as for example New Orleans, is regarded as a desirable addition to coffee. After-dinner coffee often contains it. It is best added by the consumer; if present in whole or ground coffee without a declaration it is obviously improper.

Substitutes.—At an early period coffee was roasted and ground by the consumer, but later it was sold ready ground as a convenience. This opened the way to fraud, to offset which, as well as to avoid the deterioration of ground coffee, a return to home grinding was advocated. Undaunted, the skillful imitator proceeded to make artificial coffee beans molded from suitably colored dough, sometimes, as described by Hanausek,¹ in slightly different shapes and sizes. A less skillful fraud, detected by the writers, was the addition of broken lumps of imitation coffee made from dough, rolled and roasted peas, and lumps of chicory. Glazing and coloring have also been practiced.

¹ Z. Nahr. Unters. Hyg. 1889, 3, 3.

At one time cheap grades of ground coffee often contained substitutes, notably chicory, roasted cereals, roasted peas, and various pellets and lumps made up of mixtures of these and other ingredients. This list of the common substitutes may be extended indefinitely by including those peculiar to other countries, among which are date stones, vegetable ivory, acorns, dried figs, grape pomace, seeds of wax palm (*Corypha cerifera* L.), chick peas, peanuts, lupines, coffee cassia, carob beans, and other leguminous seeds. In addition to chicory, other dried roots such as beet roots, turnips, carrots, and dandelion have been reported. These substitutes were sometimes sold under their true names to those who could not afford real coffee or could not endure its physiological action.

Detection of these materials depends on a knowledge of their structure, as noted elsewhere in this volume, and that of the coffee bean. A rough means of separation

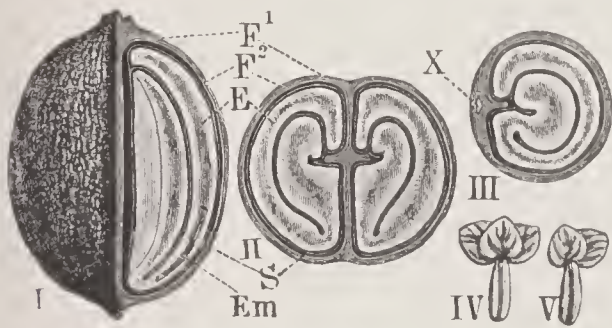


FIG. 23.

FIG. 23.—Coffee. I and II two-berry fruit in longitudinal and cross section: F^1 (gray) outer pericarp; F^2 (white line) inner pericarp; S (white line) spermoderm; E endosperm (white horny, gray mucilaginous); Em embryo. III one-berry fruit: X cavity of rudimentary berry. IV and V tri- and dicotyledonous embryos. $\times 4$. (A.L.W.)

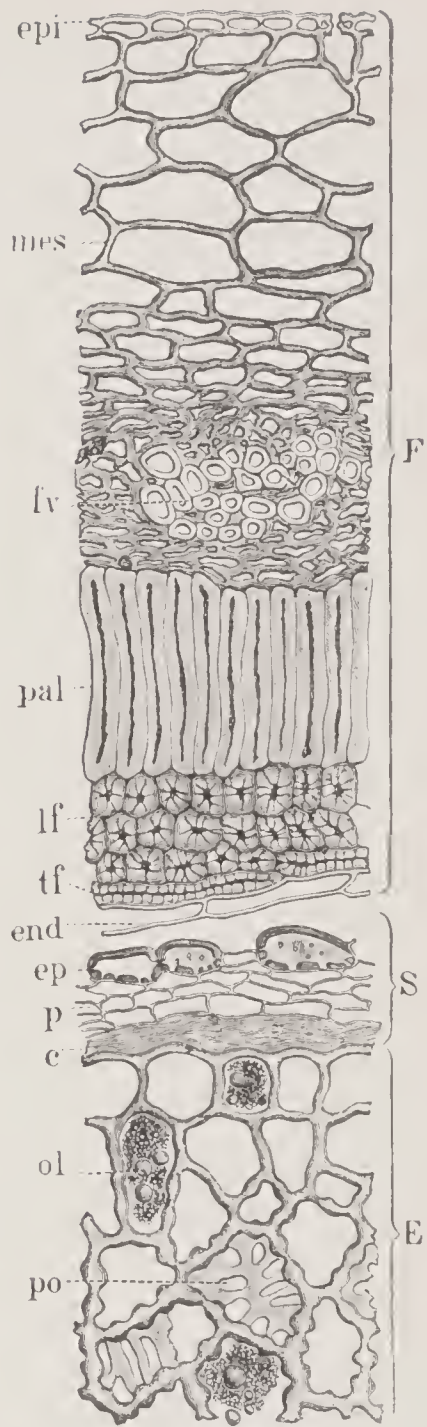


FIG. 24.

FIG. 24.—Coffee. Berry in cross section. F pericarp: epi epicarp; mes mesocarp with fv bundle; pal palisade layer; lf , tf crossing fibers; end endocarp. S spermoderm: ep epidermis with sclerenchyma cells; p parenchyma; c compressed cells. E endosperm; ol oil drops; po porous wall. $\times 160$. (A.L.W.)

is to shake ground coffee for a few seconds with cold water, whereupon the common cereals, peas, and chicory sink, while the coffee fragments, if not over roasted, float. By microscopic examination the nature of the particles in each portion is then determined.

MACROSCOPIC STRUCTURE (Figs. 23 and 24).—Noteworthy characters of the *flower* are its fragrance, the five-parted calyx adherent to the ovary, the salver-shaped, cream-colored corolla, and the two ovary cells each with an amphitropous seed. During ripening of most varieties the *fruit* (I) changes first to red, then to deep crimson or purple. It is ovoid with the slightly elevated remains of the calyx and stigma at the top. Usually both ovules develop (II), but in one-berry or pea-berry coffee (III) one *seed* is abortive, its locule (III, X) remaining minute.

The outer pericarp (F^1) is black and punky, the inner pericarp (F^2) thin, light-colored, and parchmentlike. An exceedingly thin skin, known as the "silver skin," constitutes the spermoderm. In preparing the bean before shipment all the pericarp and most of the spermoderm on the surface are removed, but the spermoderm within the cleft between the folds of the perisperm still remains. The curiously folded perisperm (E) is of a horny texture except the central tissues, in which the much-elongated embryo (Em) is embedded, which are mucilaginous.

A similar horny tissue constitutes the endosperm of date stones, kaki seeds, vegetable ivory, and some other seeds.

On soaking an unroasted bean for a few days the embryo protrudes. Normally it has two cotyledons (V), but sometimes there are three (IV).

Symmetrical and Polyembryonic Seeds.—Some authors show in cross section both seeds of the fruit folded either to the right or to the left; others show one to the right and one to the left. Fig. 23, II, is in accordance with the latter or symmetrical plan which Hanausek¹ found to be less common.

Hanausek in the same paper discusses polyembryonic seeds of coffee and shows in his plate seeds with two and three perisperms, folded one within the other, each with an embryo. As proof that these perisperms are distinct and not one mechanically separated into two or three parts, he notes that they are completely separated by double spermoderm layers. This seems conclusive evidence of his theory and equally strong evidence—although this escaped his notice—that there

¹ B. deut. bot. Ges. 1895, 13, 73.

are as many seeds as perisperms, consequently the fruit is polyspermous and not merely polyembryonic.

Varieties.—Cramer¹ describes botanical or horticultural varieties of common coffee differing in the size and form of the leaves, the size of the seeds, the number of seeds in each fruit (eight or more in Menado coffee or var. *polysperma* Burck), the color of the fruit (orange, yellow, red), and habits of the tree.

MICROSCOPIC STRUCTURE.—The entire coffee berry is practically unknown outside of the country of production, but material for study may usually be obtained from importers since a few berries escape the pulping, shelling, and polishing process and are removed previous to roasting.

All the works on pharmacognosy and food microscopy describe the structure of coffee. Of particular interest are Hanausek's studies² of the development of both the fruit and seed.

Pericarp (Fig. 24, *F*; Fig. 25).—Six layers are present: (1) *epicarp* (*epi*) of polygonal cells, with brown contents, and stomata; (2) *mesocarp* (*mes*) of thick-walled cells, also with brown contents, and collapsed cells in the inner portion, through which run the fibro-vascular bundles (*fv*); (3) *palisade cells* (*pal*) with greatly swollen walls; (4) *longitudinal sclerenchyma fibers* (*lf*); (5) *transverse sclerenchyma fibers* (*tf*); and (6) *endocarp* (*end*) of thin-walled cross cells.

Although the *fibro-vascular bundles* are in two rings in the fresh fruit, by the collapsing of the inner mesocarp cells this arrangement is not evident in the dry material. The xylem consists of numerous pitted, reticulated (*r*), and spiral (*sp*) vessels, passing into accompanying sclerenchyma cells (*sc*) and pitted cells and fibers (*pi*). Some of the fibers have diagonal pores, but their outline is usually irregular and not of the usual bast fiber type.

The crossing *fibers* of the fourth (*lf*) and fifth (*tf*) coats constitute the inner pericarp or parchment coat of the fruit. A similar tissue is that of the apple core. This material has been used as an adulterant of cattle foods.

Spermoderm (Fig. 24, *S*; Fig. 26).—The three layers, first adequately described by Hanausek, are classed as spermoderm although Houk,³ in a preliminary note, states that the ovule has no integument. They are (1) *outer epiderm* (*ep*) with sclerenchyma cells (*st*) mostly longitudinally elongated in groups between thin-walled cells (*p*); (2)

¹ Meded. Dept. Landb. 1913, Nr. 11.

² Z. Nahr. Unters. Hyg. 1890, 4, 237, 257; 1891, 5, 185, 218; 1893, 7, 85, 195.

³ Science 1936, 83, 465.

middle layer of thin-walled cells (*p*), also mostly longitudinally elongated; and (3) transversely elongated *compressed cells* (*c*).

Usually only the *outer epiderm* is clearly defined, although oxalate crystals (*cr*) are seen in the underlying layers. The epidermal *sclerenchyma cells* (*st*) are highly characteristic. Although in the commercial coffee beans the spermoderm on the dorsal (rounded) side, where the sclerenchyma cells are most strongly elongated, is largely removed in shelling and polishing, often a portion still adheres to the ventral (flattened) side and almost invariably a considerable amount is present in the cleft. In such fragments may be found sclerenchyma

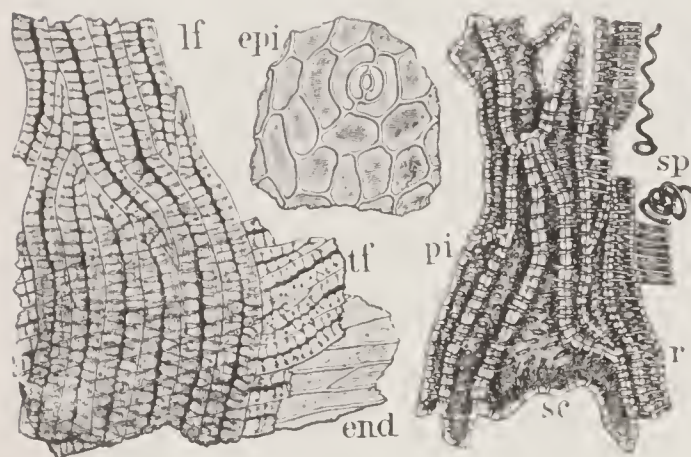


FIG. 25.

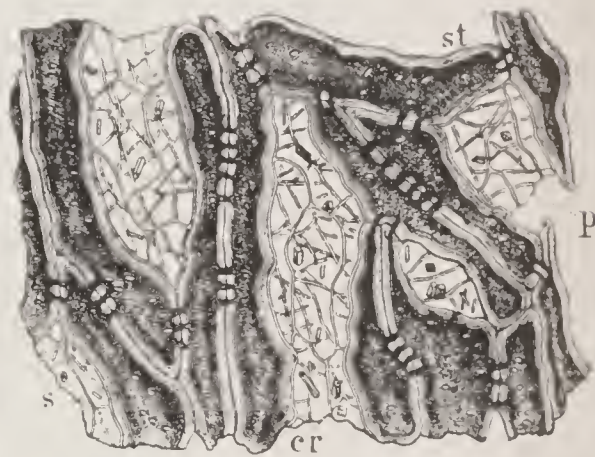


FIG. 26.

FIG. 25.—Coffee. Pericarp in surface view. *epi* epicarp; *sc* sclerenchyma cells; *pi* pitted cells; *r* reticulated vessels; *sp* spiral vessels; *lf* longitudinal and *tf* transverse fibers; *end* endocarp. $\times 160$. (A.L.W.)

FIG. 26.—Coffee. Spermoderm in surface view. *p* parenchyma and *st* sclerenchyma cells of outer epiderm; *s* subepiderm with *cr* crystals. $\times 160$. (A.L.W.)

cells of various forms, some irregular, elongated and extended in different directions, others more nearly isodiametric.

Perisperm (Fig. 24, *E*).—Houk,¹ contrary to the long current belief, has demonstrated that the bulky portion of the seed is perisperm, not endosperm. While all the walls are thickened, those of the outer layers are thinnest and of uniform structure without evident pores or beads. Proceeding inward the cells increase in size and the walls become knotty thickened, that is, they show pronounced beads separated by constrictions corresponding with the pores (*po*) seen in surface view. The wall substance is cellulose, staining blue with chlorzine iodine.

¹ Loc. cit.

The cell contents of unroasted beans consist of oil drops (*ol*) and ill-defined matter in which proteins, reducing sugars, and tannin may be detected by the usual tests. Tests for caffeine, such as the gold chloride test applied to the crystalline sublimate, are sometimes of value, although questions arising as to the presence of caffeine generally may be best answered by the results of quantitative determination. Netolitzky¹ notes the presence of crystals of calcium oxalate.

Endosperm.—The dark tissues extending through the middle of the folds of the perisperm, best seen in unroasted beans, consist of ill-defined cells with mucilaginous lamellæ which dissolve in water leaving only the thin middle lamella. In this tissue is embedded the embryo. The classification as endosperm is tentative.

Embryo.—By careful dissection of a bean, softened by soaking, the embryo may be separated. If allowed to soak for some days in water, the embryo swells and breaks through the endosperm as in sprouting. The cells are small and characterless.

CHIEF STRUCTURAL CHARACTERS.—Fruit ovoid, normally two-celled, two-seeded. Outer pericarp soft, inner pericarp parchmentlike. Spermoderm papery. Perisperm folded, horny. Embryo minute.

Outer pericarp of polygonal epicarp cells, thick-walled mesocarp with vascular bundles, and palisade cells; inner pericarp of crossing sclerenchyma fibers and thin-walled endocarp. Spermoderm with groups of sclerenchyma cells. Perisperm with knotty thickened walls.

CHEMICAL COMPOSITION.—Raw coffee, besides water, contains protein, the alkaloids caffeine and coffearine, oil, sugar, dextrins, pentosans, cellulose, “caffetannic acid” (chlorogenic and coffalic acids), ash, and various acids and minor constituents.

Influence of Roasting on Composition.—Roasting drives off most of the water, caramelizes a large part of the sugar, reduces the *caffetannic acid* by about half, and develops the coffee aroma. A slight loss of *caffeine* usually takes place. The splitting of chlorogenic acid into caffeic and quinic acids, and of these latter into other substances, is considered below under Constituents. The physical nature of the bean is also altered by roasting, the raw bean being tough and horny, whereas the roasted bean is brittle.

Bernheimer² identified as the products of roasting: *caffeol*, *palmitic acid*, *acetic acid*, *carbonic acid*, *hydroquinone*, *pyrrol*, *acetone* (?), and *methylaniline*. He found in the roasted product: fatty acids

¹ Z. Unters. Nahr.-Genussm. 1910, 20, 221.

² Monatsh. 1880, 1, 456.

0.48, caffeine 0.18, and caffeol 0.05 per cent. Jaeckle¹ found that considerable *furfural* and *acetic acid* resulted from the roasting, also traces of *formic acid*, *furfuran*, *ammonia*, *trimethylamine*, *acetone*, and *resorcin*, but was unable to isolate the caffeol of Bernheimer. He and several other authors have recorded a slight loss of caffeine during roasting, but, as noted below, the nature of the chief odorous constituent is in controversy.

Schwartz and Wagner,² in a series of experiments involving determination of shrinkage, water, sugar, caramel, and fat values of Bogota coffee, obtained the best flavor by roasting rapidly at a high temperature.

Orosco³ recognizes four reactions produced in heating coffee as follows: (1) elimination of hygroscopic and loosely bound water, reaching a maximum at 100° C., but diminishing to 240° C.; (2) destruction of invert sugar reaching a maximum at 160° C., decreasing to 290° C. with a sharp break at 230° C.; (3) decomposition of chlorogenic acid reaching a maximum at 230° C., then decreasing to 300° C.; and (4) decrease in nitrogen-free extract beginning above 110° C., and most active between 130 and 170° C., followed by an increase reaching a maximum at 280° C.

In the table given on p. 149 are analyses of coffee reported by Bell,⁴ Warnier,⁵ Kisch,⁶ and Kissling,⁷ the figures credited to Kissling being from a pamphlet by Wimmer, who apparently combined the results of several chemists. Although some of the figures are open to criticism and most of the analyses are not so complete as might be desired, they bring out well certain details and supplement the comprehensive analyses of roasted coffee by Lythgoe as given in the table on the following page which are particularly valuable in differentiating coffee from its substitutes.

Juckenack and Hilger⁸ in comparative analyses brought out a slight loss of *caffeine* and *fat* due to ordinary roasting. When, however, the roasting was carried out with addition of 8 to 9 per cent of sugar a loss of about 40 per cent of the caffeine and 10 per cent of the fat was noted.

¹ Z. Unters. Nahr.-Genussm. 1898, **1**, 457.

² Rensselaer Polytech. Inst. Bul. Eng. Sci. Series 1935, No. 51.

³ Rev. chim. ind. (Rio de Janeiro) 1936, **5**, 98.

⁴ Chemistry of Foods, London, 1881 and 1883.

⁵ Pharm. Weekbl. 1899, No. 13.

⁶ König: Chem. mensch. Nahr.-Genussm. 1903, **1**, 986.

⁷ Chem. Ztg. 1908, **32**, 495.

⁸ Forsch. Lebensm. 1897, **4**, 119.

COMPOSITION OF RAW AND ROASTED COFFEE

	Water	Pro- tein*	Caf- feine	Fat†	N-f. Ext.	Sugar	Dex- trin	Pento- sans	Fiber	Caffe- tannic acid	Ash
	%	%	%	%	%	%	%	%	%	%	%
Bell											
Mocha:											
Raw.....	8.98	9.87‡	1.08	12.60	9.55	0.87	8.46	3.74
Roasted....	0.63	11.23‡	0.82	13.59	0.43	1.24	4.74	4.56
E. Indian:											
Raw.....	9.64	11.23‡	1.11	11.81	8.90	0.84	9.58	3.98
Roasted....	1.13	13.13‡	1.05	13.41	0.41	1.38	4.52	4.88
Kisch											
Java:											
Raw.....	13.81	12.20	1.48	12.17	39.75§	7.40	16.61	3.98
Roasted....	1.92	15.74	1.44	16.51	41.06	2.45	18.42	4.91
Kissling											
Raw.....	10.73	11.57	1.07	11.80	37.80	7.62	0.86	24.01	9.02	3.02
Roasted....	2.38	12.97	1.16	13.85	47.13	1.31	1.31	18.07	4.63	4.65
Warnier											
<i>C. arabica</i> :											
Raw.....	11.24	15.74	1.16	13.63	25.02	5.14	28.75	4.46
Roasted....	5.64	14.71	1.57	14.20	38.58	3.15	20.47	4.83
<i>C. liberica</i> :											
Raw.....	11.40	14.43	1.59	12.19	29.69	5.01	26.68	4.02
Roasted....	3.98	14.42	2.19	13.13	46.59	2.44	15.32	4.37

* Caffeine deducted. † Ether extract. ‡ "Legumin and albumin."

§ Water extract 23.84%. || Water extract 24.42%.

Fresenius and Grünhut¹ secured results on the dry basis showing an average of about 10 per cent less *ether extract* in 4 samples of coffee roasted with 7.5 and 9 per cent of *sugar* than when no sugar was added, but the average *caffeine* content in 2 samples was less and in 2 samples more in the sugar-roasted product. They do not agree with the conclusion of König² that the sugar-roasted product is inferior because of the lower content of ether extract.

Lythgoe's analyses of roasted coffee³ were originally published in a single table but are here given in two tables. For comparison with foregoing results the figures on nitrogen given by the author are calculated to protein after deduction of nitrogen present in the caffeine. Results on nitrogen-free extract are not tabulated by the author, but calculation shows that they vary from 49.29 to 55.74, average **53.83** per cent.

¹ Z. anal. Chem. 1897, **36**, 225.

² Z. angew. Chem. 1888, **1**, 632.

³ Tech. Quart. 1905, **18**, 236.

COMPOSITION OF ROASTED COFFEE AND SUBSTITUTES (LYTHGOE)

	Water	Pro- tein*	Caf- feine	Fat†	Red. Sugar	Starch‡	Fiber	Ash, total	Ash, sol.	Ash, alk.§	Cl	Sol. P ₂ O ₅	Insol. P ₂ O ₅
	%	%	%	%	%	%	%	%	%	cc.	%	%	%
Santos	1.40	11.88	1.25	14.58	0.52	2.28	13.41	4.16	3.46	2.97	0.02	0.32	0.35
"	1.87	12.12	1.10	13.84	0.68	1.00	11.02	4.31	3.62	3.36	0.02	0.29	0.30
"	1.31	12.75	1.20	13.86	0.75	2.32	14.71	3.80	3.00	3.35	0.02	0.27	0.30
P. Rico	1.29	11.81	1.38	13.00	0.50	2.17	13.11	4.05	3.30	3.53	0.02	0.31	0.34
"	1.26	11.94	1.21	13.34	0.63	1.58	12.93	4.06	3.27	3.72	0.02	0.23	0.35
"	1.48	12.19	1.32	14.12	0.54	2.62	12.50	4.12	3.32	3.66	0.02	0.33	0.33
Rio	1.76	11.44	1.11	13.38	0.68	2.82	14.08	4.06	3.40	4.16	0.02	0.21	0.17
"	2.34	11.63	1.10	13.71	0.78	1.47	13.10	3.91	3.24	3.17	0.02	0.36	0.23
"	2.10	12.00	1.17	13.53	0.61	2.62	11.91	3.74	3.06	3.22	0.02	0.36	0.24
Mocha	2.05	12.13	1.16	14.84	1.78	2.30	11.22	4.05	3.25	3.94	0.02	0.28	0.35
"	2.95	10.69	1.00	14.47	0.94	1.85	12.34	3.85	3.07	3.26	0.02	0.33	0.36
"	2.40	10.50	1.18	15.18	1.42	2.90	13.20	3.80	3.00	3.54	0.01	0.34	0.55
Java	3.34	13.06	1.34	12.61	0.32	2.95	13.43	4.09	3.27	3.88	0.02	0.26	0.42
"	3.35	12.31	1.30	12.28	0.42	2.32	13.77	4.38	3.56	3.54	0.02	0.19	0.39
"	3.44	13.75	1.27	13.54	0.66	3.34	14.75	3.96	3.10	2.95	0.01	0.24	0.38
Min.	1.29	10.50	1.00	12.28	0.32	1.00	11.02	3.74	3.00	2.95	0.01	0.19	0.17
Max.	3.44	13.75	1.34	15.18	1.78	3.34	14.75	4.38	3.62	4.16	0.02	0.36	0.55
Aver.	2.16	12.00	1.20	13.75	0.75	2.30	13.03	4.03	3.26	3.55	0.02	0.29	0.33
Wheat	5.60	11.50	0.00	2.40	4.10	28.58	6.23	5.71	2.82	0.34	0.65	1.46
Chicory	5.55	6.88	0.00	0.88	19.34	2.10	5.91	4.37	2.27	0.95	0.08	0.28	0.31

* Total N less caffeine N \times 6.25. †Petroleum ether extract. Refractive index of the extract 1.4750 to 1.4760. ‡Reducing matters by diastase method; not true starch. §Cc. N/10 acid per 1 gram of coffee.

Lythgoe's figures on the alkalinity of the ash, calculated in terms of cc. N/10 acid per gram of the ash itself, range from 71.4 to 102.3 for roasted coffee; for roasted wheat and roasted barley they are respectively 6.0 and 21.8. Röszenyi¹ obtained similar results on the ash of other cereals, thus: barley 5.1, glazed rye 5.6, and ground wheat 9.0 cc. per 1 gram of ash. This determination is of value in estimating quantitatively the cereal admixture in coffee, thus confirming microscopic examination and iodine tests of the liquid obtained by boiling the finely ground sample with water.

Staling of Coffee and Vacuum Packing.—Abelin and Perelstein's experiments² appear to indicate that when raw coffee is treated with water vapor under a pressure of 4.5 atmospheres and distilled *in vacuo* (Asa process) volatile substances are removed which render the infusion less toxic. Gould³ observed that coffee packed in a container

¹ Chem. Ztg. 1913, **37**, 1482.

² Münch. med. Wochschr. 1914, **61**, 867.

³ 8th Int. Cong. App. Chem. 1912, **26**, 389.

EXTRACTIVE MATTER OF ROASTED COFFEE AND SUBSTITUTES (LYTHGOE)

	Cold water extract	Alcohol extract	Ten Per Cent Extract *				
			Sp. gr. 15° C.	Refraction † 20° C.	Ref. ind. 20° C.	Solids	Ash
	%	%				%	%
Santos.....	20.80	16.83	1.0107	26.7	1.33770	2.64	0.40
“.....	22.72	17.11	1.0108	26.9	1.33777	2.64	0.39
“.....	21.70	17.80	1.0101	26.0	1.33743	2.46	0.30
Puerto Rico	22.48	15.70	1.0107	26.6	1.33766	2.60	0.37
“.....	21.76	16.36	1.0104	26.3	1.33754	2.50	0.36
“.....	24.44	16.91	1.0113	27.6	1.33804	2.77	0.30
Rio.....	22.66	17.00	1.0103	25.5	1.33724	2.48	0.40
“.....	22.61	17.34	1.0101	25.8	1.33735	2.46	0.36
“.....	22.75	17.37	1.0101	26.0	1.33743	2.46	0.30
Mocha.....	24.00	18.01	1.0106	26.4	1.33758	2.65	0.40
“.....	20.27	17.96	1.0101	26.3	1.33754	2.47	0.36
“.....	24.18	19.55	1.0111	27.3	1.33793	2.72	0.40
Java.....	23.85	15.95	1.0110	26.9	1.33777	2.63	0.39
“.....	22.19	15.45	1.0107	26.5	1.33762	2.58	0.38
“.....	23.20	16.21	1.0108	26.6	1.33766	2.62	0.38
Min.....	20.27	16.45	1.0101	26.0	1.33743	2.46	0.30
Max.....	24.44	19.55	1.0113	27.6	1.33804	2.77	0.40
Aver.....	22.63	17.03	1.0105	26.6	1.33766	2.72	0.37
Wheat.....	25.88	10.72
Chicory.....	72.92	34.39	1.0307	45.0	1.34463	7.44	0.26

* Boiled 1 hour as described by McGill (Trans. Roy. Soc. Canada 1887).

† Immersion refractometer reading.

and exhausted to 183 mm. pressure gave off gas sufficient to overcome the pressure and produce 253 mm. additional, while coffee packed under normal pressure gave off only enough to produce the additional pressure. The gas from the vacuum-packed coffee container had 81.1 per cent of carbon dioxide and 4.6 per cent of carbon monoxide, while that packed at ordinary pressure had 62.8 per cent of carbon dioxide and 4.7 per cent of carbon monoxide. According to Gould, the decomposition products are: (1) sucrose and the mother substance of a fixed oil, (2) a glucosidelike substance formed from the sucrose, and (3) probably a caramel compound which in turn decomposes into the gases.

The 50 to 100 per cent increase in volume of coffee during roasting is due, according to Punnett and Balart,¹ to the formation of carbon

¹ Tea Coffee Trade J. 1934, 37, 428.

dioxide (90 to 95 per cent) together with a small amount of carbon monoxide which distend the cells at a pressure of about 100 pounds per square inch. Vacuum sealing neither "pulls" the gas from the coffee nor injures the flavor.

Bengis¹ attributes the staling of coffee to slow oxidation of the oil containing the substances that contribute flavor, which takes place even in vacuum-packed cans. In aging experiments carried out with whole roasted beans, the fat extracted with petroleum ether showed a drop of the *iodine number* (Hanus) in 12 months from 96.05 to 95.65 and of the *saponification number* from 172.08 to 171.90, but a rise of the *Reichert-Wollny number* from 0.866 to 1.973. Still more striking differences were brought out by the determination of the *oxidizability number*, employing a modification of Issoglio's method, in which potassium dichromate was substituted for potassium permanganate. Portions of a sample showed on aging in tight jars the following oxidizability numbers: fresh 141, aged 10 days 102.4, aged 20 days 94.5, and aged 4.5 months 78.3; in another portion aged for 12 months in an open sack, the number dropped to 32.2. Vacuum packing reduced, but did not prevent, these changes; in 12 months the iodine number of a lot of whole beans dropped from 95.87 to 93.27, the oxidizability number from 111.8 to 91.3, and the Reichert-Wollny number rose from 0.925 to 2.321. In the first 6 days a distinct drop in oxidizability value was noted.

Punnett² states that only 5 cc. of air remains in a 1-pound can of vacuum-packed coffee and the off-flavor due to this is only 2.5 per cent, which is scarcely evident to an expert. Deterioration of coffee not so protected develops normally in 9 to 10 days.

Among the substances listed by Staudinger and Reichstein³ as obtained from roasted coffee by vacuum distillation are: *acetaldehyde*, *furan*, *furfuraldehyde*, *furfuryl alcohol*, *pyridine*, *hydrogen sulphide*, *diacetyl*, *methyl mercaptan*, *furfuryl mercaptan*, *dimethyl sulphide*, *acetylpropionyl*, *acetic acid*, *guaiacol*, *vinyl guaiacol*, *pyrazine*, and *n-methylpyrrole*.

The mixed volatile constituents, as separated by Prescott, Emerson, and Peakes,⁴ were found to be very unstable. The fact that the furfuryl alcohol fraction is unstable, when slightly acid, suggests that this and possibly other non-fatty constituents in roasted coffee are

¹ Food Ind. 1935, 7, 490; Ind. Eng. Chem. 1936, 28, 290.

² Food Ind. 1936, 8, 178.

³ British Patents 246,454 and 260,960.

⁴ Food Res. 1937, 2, 1.

factors in staling. When coffee is stored in air, particularly if moist, staling develops rapidly.

Prescott, Emerson, Woodward, and Heggie¹ do not attribute the staling of coffee wholly to products of oxidative rancidity of the fats which of themselves contribute neither flavor nor aroma. One of the products of roasting is *p*-vinyl guaiacol, formed from chlorogenic acid, which, being readily oxidized, is believed to contribute odor, as do also, as noted by Staudinger and Reichstein, the *terpenes* and the *organic sulphur compounds* of the heterocyclic mercaptan series. *Furfuryl alcohol*, although formed during roasting, is not present in the water infusions of aged coffee. Of the constituents found by these authors, *acetic acid*, *furfuryl alcohol*, *furfuraldehyde*, *p*-vinyl guaiacol, *diacetyl*, *kahweol*, and *guaiacol* had been reported previously by other workers, whereas *p*-vinylcatechol, *formic acid*, *vanillone*, *n*-heptacosane, *silvestrene*, *eugenol*, *diethyl ketone*, and a *hydrocarbon* melting at 116 to 117° C. had not been mentioned.

The substances named above by Staudinger and Reichstein are stated not to exist as such in the coffee, being decomposition products obtained during analysis; however, Johnston and Frey² actually obtained the first 7 on the list by high vacuum distillation, also *methylacetylcarbinol*, not previously reported. They confirm the conclusions of Prescott and associates that "coffee staling is probably concerned with changes in the volatile aroma and flavor substances and does not involve fat rancidity."

Elder³ found that fat oxidation held off for 13 weeks; staling, however, appeared in 2 weeks of air storage, but was prevented by vacuum packing.

• **Caffeine-Free Coffee.**—Examination of Kaffee Hag, reported by Baird,⁴ showed that caffeine was absent. Wiley (press clipping) states that Dekofa contains only 0.15 per cent of caffeine, which is as near complete removal as can be obtained. About the same amount is present in Sanka, judging from the claim that 97 per cent has been removed. Murray⁵ notes that the Gorter method, when employed for small amounts, may give results much too high, and that purification is essential in applying the Lendrich and Nottbohm method.

Tannin-Free Coffee.—Determination of *caffetannic acid* by

¹ Ibid. p. 165.

² J. Am. Chem. Soc. 1938, 60, 1624.

³ Ind. Eng. Chem. 1937, 29, 267.

⁴ N. Dakota Agr. Exp. Sta. 1927, Bul. 17, 40.

⁵ J. Ind. Eng. Chem. 1913, 5, 668.

Howard¹ in three brands, claimed to be free from tannin, showed 10.76, 11.04, and 7.61 per cent and of caffeine 1.17, 1.33, and 0.87 per cent. In coffee chaff 5.98 per cent of caffetannic acid and 0.40 per cent of caffeine were present, thus showing the absurdity of the manufacturer's claim that by its removal the tannin was diminished.

Shanley² in 3 brands each of "tanninless" and ordinary coffee found respectively an average of 9.77 and 9.65 per cent of caffetannic acid and 1.12 and 1.17 per cent of caffeine. The average of caffetannic acid in the chaff of the coffee was 6.60. The chaff in the coffee varied from 1.77 to 2.38, aver. **1.98** per cent.

Coffee Extracts.—Rouillard³ found in a commercial dry extract of coffee: water 3.65, reducing substances 2.60, and caffeine 2.45 per cent. His experiments showed that there was a considerable loss of caffeine in its preparation.

Coffee Substitutes.—Woods and Merrill⁴ examined 8 cereal substitutes made and sold in the United States with the following results: soluble protein 1.4 to 5.6, soluble carbohydrates 13.4 to 44.9, soluble ash 1.5 to 4.1, and total soluble solids 22.4 to 51.2 per cent. Comparison of the composition of the infusion prepared according to directions with that of skim milk shows that the latter contains much more carbohydrates and ash and at least ten times as much protein.

See also Coffee Cassia, Chicory, and Dandelion. Analyses of roasted chicory and wheat appear in the two foregoing tables.

Numerous analyses of European substitutes made mostly prior to 1890 are given by König.⁵

CONSTITUENTS.—Purine Bases.—See also Introduction to Part II.

Caffeine.—Gorter⁶ holds that the caffeine of coffee is wholly combined with chlorogenic acid; Lendrich and Nottbohm⁷ consider that it exists free.

Passing over earlier analyses, the following minimum and maximum results have been reported by the authors named: Siedler,⁸ 18 samples from German and Portuguese colonies, 0.91 to 2.36 per cent; Lythgoe (see above) 1.00 to 1.38 per cent; Hefelmann,⁹ numer-

¹ U. S. Dept. Agr., Bur. Chem. 1907, Bul. **105**, 41.

² Connecticut Agr. Exp. Sta. Rep. 1907, p. 141.

³ Ann. fals. 1914, **7**, 441.

⁴ Maine Agr. Exp. Sta. 1900, Bul. **65**, 103.

⁵ Chem. mensch. Nahr.-Genussm., Berlin, 1903, **1**, 997 and 1509.

⁶ Ann. 1911, **379**, 110.

⁷ Z. Unters. Nahr.-Genussm. 1909, **17**, 241.

⁸ Ber. deut. Pharm. Ges. 1898, **8**, 19.

⁹ Z. öffent. Chem. 1908, **14**, 448.

ous samples of raw coffee, 0.86 to 1.67 per cent; Lendrich and Nottbohm,¹ South American raw, 0.96 to 1.25, roasted 1.19 to 1.44, Central American raw 1.02 to 1.55, roasted 1.15 to 1.50, Asiatic raw 1.07 to 1.51, roasted 1.16 to 1.72, African raw 0.97 to 2.60, roasted 1.16 to 3.00 per cent. The experiments of Herndlhofer² brought out that the caffeine content increases, largely at the expense of the nitrogen-free extract, during the drying as well as the ripening. Nottbohm and Mayer³ give 1.06 to 1.29 per cent as the range for common coffee and 1.24 to 2.22 for wild coffee. See Trigonelline below.

Coffearine, $C_{14}H_{16}O_4N_2$.—This alkaloid, discovered by Palladino⁴ and for a time a subject for controversy, appears to have been definitely isolated by Graf⁵ by the following method: extract finely ground coffee with milk of lime, precipitate the solution with lead subacetate, filter, delead the filtrate with sulphuric acid, and extract the caffeine with chloroform. Precipitate the coffearine with potassium bismuth iodide, and liberate the alkaloid with silver oxide. Coffearine crystallizes as needles melting at 140° C.

Choline Bases. *Choline*, $C_5H_{15}NO_2$.—In Santos coffee, Nottbohm and Mayer⁶ found 0.022 per cent of choline.

Trigonelline, $C_7H_7NO_2$.—Nottbohm and Mayer⁷ give as the range in common coffee 0.228 to 0.245 and in wild coffee 0.110 to 0.198 per cent, the ratio of caffeine to trigonelline being in the former case about twice that in the latter. Roasting, even at 250° C. and decaffeinating cause no loss of trigonelline. Heiduschka and Brüchner⁸ describe the preparation of trigonelline sulphate from Guatemala coffee in a form identical with that prepared from nicotine. It is soluble in hot water and hot alcohol, but insoluble in ether and chloroform. Hydrochloric acid changes it at 265° C. into nicotinic acid.

Other Nitrogenous Substances.—Bernheimer⁹ noted the presence of pyrrol (C_4H_5N) in roasted coffee. Bertrand and Weisweiler¹⁰ obtained from the steam distillate of 5 kilos of roasted coffee an aqueous liquid having the mixed odor of coffee, pyridine (C_5H_5N), fur-

¹ Z. Unters. Nahr.-Genussm. 1909, **18**, 299.

² Z. Unters. Lebensm. 1933, **65**, 561.

³ Ibid. 1931, **61**, 429.

⁴ Gaz. chim. ital. 1895, **25**, 104.

⁵ Z. öffent. Chem. 1904, **10**, 271.

⁶ Z. Unters. Lebensm. 1932, **63**, 176.

⁷ Ibid. 1931, **61**, 429.

⁸ J. prakt. Chem. 1931, **130**, 11.

⁹ Loc. cit.

¹⁰ Compt. rend. 1913, **157**, 212.

fural, and *amyl alcohol*. From this 1 to 2 cc. of an oil was separated, and from the oil pyridine equivalent to 0.2 to 0.5 gram per kilo of coffee was obtained. Sayre¹ has also obtained pyridine from roasted coffee.

Fixed Oil. *Physical and Chemical Values.*—The fatty oil obtained by extraction with petroleum ether, has been examined by several authors. De Nigri and Fabris² and Schuette, Cowley, and Chang³ extracted only the raw beans, the last-named authors removing with tetrachloroethane the surface wax (0.24 per cent) preliminary to dissolving the oil (2.7 per cent). In order to study the effects of roasting, Hilger and Juckenack⁴ and Heiduschka and Kuhn⁵ made comparative analyses of the fat of both raw and roasted beans. Bengis and Anderson⁶ studied the influence of aging on the fat (petroleum ether extract) of roasted beans.

VALUES OF OIL OF RAW AND ROASTED COFFEE

	Sp. gr. 15° C.	Ref. index 25° C.	Solid. pt.	Sapon. No.	Iodine No.	Reichert- Meissl No.	Polen- ske No.	Hehner No.	Acid No.	Unsap. Matter
DeN. and F.:			C°							%
Raw:										
Min.....	0.9510	+3	165.0	79.0
Max.....	0.9520	+6	173.0	87.0
H. and J.:										
Raw.....	1.4750		157.2	82.4	0.	4.1	6.87
Roasted.....	1.4770		162.7	84.0	0.34	5.5	6.08
H. and K.:										
Raw.....	1.4767	+4.5	175.0*	86.8	0.08	96.9	5.33	1.96
Roasted.....		173.9*	93.5	7.93
B. and A.:										
Roasted:										
Fresh.....		172.1	96.0	0.87†	10.2
Aged 12 mo.....		171.9	95.6	1.97†	9.6
S., C., and C.:										
Raw.....	0.9717	1.4790	195.5	100.7‡	0.36	0.4§	7.05	12.63

* Ester No., i.e., saponification No. less acid No. †Reichert-Wollny No. ‡ Wijs. Iodine No. of fatty acids 94.1. Thiocyanogen No. 91.6. Hydroxyl No. 22.8. § Saturated acids 33.6%; unsaturated acids 38.0% (Iodine No. 153.6). || Iodine No. 154.

¹ Bul. Pharm. 1916, **30**, 276.

² Z. anal. Chem. 1894, **33**, 569.

³ J. Am. Chem. Soc. 1934, **56**, 2085.

⁴ Forschungs-Ber. Lebens. 1895, **2**, 223.

⁵ J. prakt. Chem. 1934, **139**, 269.

⁶ J. Biol. Chem. 1934, **105**, 139; Ind. Eng. Chem. 1936, **28**, 290.

The *refractive index* of the fat of unroasted coffee as found by Spaeth ¹ was 1.4777 to 1.4778 and by V. Noel ² in 6 samples 1.4767 to 1.4774, in both cases recalculated to 25° C. Bengis and Anderson ³ conclude that aging and roasting alone do not materially affect the fat, but aging following roasting caused the changes noted in the foregoing and following tables.

Composition.—The calculated percentages of fatty acids obtained by Meyer and Eckert,⁴ by V. Noel, by Heiduschka and Kuhn, by Bengis and Anderson, and by Schuette, Cowley and Chang follow:

	M. and E. Raw	V. N. Raw	H. and K. Raw	B. and A.		S., C. and C. Raw
				Fresh Roasted	Aged Roasted	
	%	%	%	%	%	%
Carnaubic acid....	10	14	14.3	1.8*	1.9*
Arachidic acid....	2.1
Stearic acid.....	1.0	6.4	7.4	9.1
Daturic acid.....	1– 1.5	3
Palmitic acid.....	25–28	29	23.6	29.2	28.1	20.2
Myristic acid.....	2.2
Capric acid.....	0.5	0.3
Oleic acid.....	2	2	20.2	20.9	23.8	12.4
Linolic acid.....	50	50	37.6	29.5	27.0	25.7
Unsapon. matter..	21.2	6.5–13.4	2.0	10.2	9.7	~ 12.6

* Given as tetracosanic acid with the statement that it is probably identical with carnaubic acid.

The analyses in the table show reasonable agreement in the percentages of palmitic acid and the sum of the oleic and linolic acids, but a divergence of other figures. The footings indicate that the results on acids in the first three columns are percentages of the total fatty acids alone, free from unsaponifiable matter and glycerin.

Meyer and Eckert ⁵ found 21.2 per cent of nitrogen-free unsaponifiable *wax* which gave a phytostearin reaction and, judging from the saponification and oxidation reactions, was a *tannol carnaubate*. The carnaubic (tetracosanic) acid of Bengis and Anderson appears to have

¹ Chem. Ztg. 1895, **31**, 292.

² Pharm Zentralh. 1929, **70**, 69.

³ Loc. cit.

⁴ Monatsh. 1910, **31**, 1227.

⁵ Loc. cit.

come from the wax which Schuette, Cowley, and Chang extracted from the surface.

From methanol and acetone solutions of the unsaponifiable matter, Bengis and Anderson¹ crystallized *kahweol*, $C_{19}H_{26}O_3$, melting at 143 to 143.5° C. and rotating $[\alpha]$ at 21° C. -204.5° , a highly unsaturated substance, readily decomposed by light, heat, and mineral acids. These authors also isolated a phytosterol similar to sitosterol.

Volatile Oil.—Bernheimer² obtained from coffee, by distillation, extraction of the distillate with ether, evaporation of the ether, and fractionation of the residue, an oily substance which he named *caffeoil* and to which he ascribed the formula $C_8H_{10}O_2$. This alleged compound was long considered the constituent to which coffee owes its characteristic aroma until Jaeckle² announced his inability to confirm Bernheimer's conclusions.

Erdmann³ obtained from roasted coffee, by steam distillation, a heavy oil (sp. gr. 1.08) containing over 3 per cent of nitrogen. An ether solution of the oil, shaken with 10 per cent sodium carbonate, gave up to the latter *acetic acid* and *valerianic acid*; the remaining oil, on fractioning, yielded about 50 per cent of *furfuralcohol* (68 to 73°), about 10 per cent of a colorless oil (86 to 102°) containing 9.6 per cent of nitrogen with a strong coffee odor, also *phenols* (112 to 130°). An odor like that of the nitrogenous fraction was obtained by heating a mixture of caffeine, "caffetannic acid," and sucrose. Erdmann states that the nitrogenous oil is physiologically active and the furfuralcohol is strongly toxic.

Gorter⁴ was unable to isolate the substance to which coffee owes its characteristic flavor; Grafe,⁵ however, verified Erdmann's findings

Other Volatile Constituents.—See pp. 152 and 153.

Organic Acids.—Certain grades of coffee beans have a characteristic flavor designated in the trade as "acid," but whether this acidity is due wholly to the *acetic acid* and traces of *formic acid* developed during roasting does not appear to have been carefully investigated. An acid so volatile as acetic would hardly be expected to remain in considerable quantity in the bean after roasting. *Chlorogenic* and *coffalic acids*, whether or not combined with the caffeine, have a bitter rather than an acid flavor. Warnier⁶ has determined the water and alcohol extracts and their acidity with the following results: water extract 26.98 to 39.92 per cent and acidity of water extract of 100 grams

¹ J. Biol. Chem. 1932, **97**, 99.

² Loc. cit.

³ Ber 1902, **35**, 1846.

⁴ Loc. cit.

⁵ Monatsh. 1912, **33**, 1389.

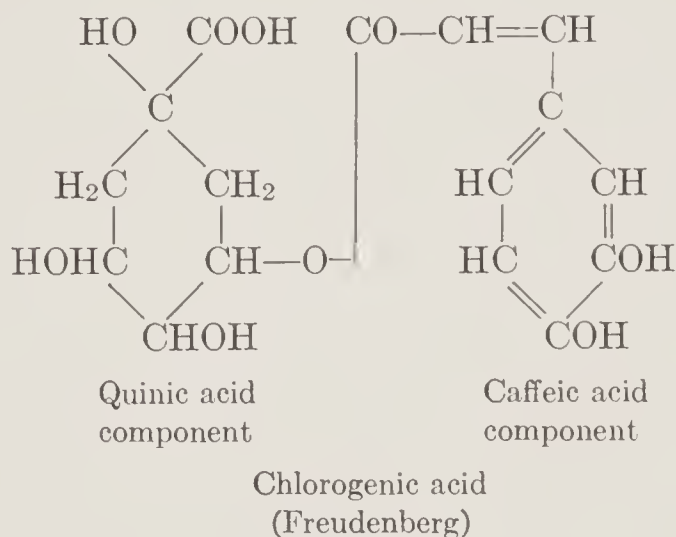
⁶ Loc. cit.

of coffee 13.9 to 33.4 cc. *N* alkali (?); alcohol extract 16.60 to 19.91 per cent and acidity of alcohol extract of 100 grams of coffee 6.6 to 11.3, cc. *N* alkali (?).

Herndlhofer,¹ who examined all parts of the coffee tree for acids, states that the fruit contains the smallest amounts of *malic* and *oxalic acids* which are located entirely in the shell. Arbenz² reports 0.08 per cent of oxalic acid in roasted coffee, and Widmark and Ahldin³ found 0.04 per cent.

Chlorogenic Acid, $C_{16}H_{18}O_9 + \frac{1}{2}H_2O$.—The caffetannic acid of earlier writers has been shown by Gorter⁴ to be a mixture of chlorogenic acid and *caffalic acid*, a new substance. Freudenberg⁵ demonstrated that chlorogenic acid is a depside of caffeic and quinic acids, juncture being between the carboxyl group of the former and one of the hydroxyl groups of the latter, and that the number of atoms in the molecule is only half that of Gorter's formula.

Fischer and Dangschat⁶ confirmed Freudenberg's formula.



Gorter obtained crystalline potassium caffeine by extracting coffee with alcohol (sp. gr. 0.9) and evaporating under diminished pressure. After acidifying with sulphuric acid, the caffeine was extracted with chloroform and the chlorogenic acid obtained in a pure state. Contrary to the view of Lendrich and Nottbohm that the caffeine of

¹ Biochem. Z. 1933, 259, 168.

² Mitt. Lebensm. Hyg. 1917, 8, 98.

³ Biochem. Z. 1933, 265, 241.

⁴ Ann. 1907, 358, 327; 1908, 359, 217; 1910, 372, 237; 1911, 379, 110.

⁵ Ber. 1920, 53, 232.

⁶ Ber. 1932, 65, 1037.

coffee is not in combination with an acid, Gorter believed that it exists entirely as the *potassium caffeine chlorogenate*. Plücker and Keilholz¹ found that 84 per cent of the chlorogenic acid existed as the potassium caffeine salt, the remainder consisting of equal parts as the potassium salt and the free acid.

Chlorogenic acid melts at 206 to 207° C. and polarizes -33.1° at 25° C. Although it gives some of the reactions of tannic acid it does not precipitate albumin, gelatin, or antipyrine, and therefore "caffetan-ic acid" is a misnomer. It is hydrolyzed by alkalies into *caffeic acid*, $C_9H_8O_4$ or $C_6H_3(OH)_2(CH:CHCOOH)$, and *quinic acid*, $C_7H_{12}O_6$ or $C_6H_7(OH)_4COOH$.

Tiedcke² decomposed chlorogenic acid, by heating under pressure in water vapor, into caffeic and quinic acids. The last two on further heating he decomposed with the evolution of carbon dioxide and the formation of *tetrahydroxycyclohexane* and *dihydroxystyrene*.

Chlorogenic acid is further stated by Gorter³ to be present in numerous species of plants belonging to a number of families. It was found in 98 out of 230 species examined, including the seeds of *Helianthus*, *Strychnos*, etc. The latex of *Castilloa elastica* and *Ficus elastica* also contain it.⁴ If 10 grams of the plant substance containing the acid are extracted with hot 8 per cent hydrochloric acid, the filtrate shaken out with ether, the latter washed with sodium bicarbonate solution and with water, and finally shaken with very dilute ferric chloride, the ether solution, if not too concentrated, becomes yellow and the aqueous liquid violet.

Hoepfner⁵ detects 1 part of *caffeic acid* in 100,000 by the vermilion color developed in acetic or phosphoric acid solution with sodium nitrite. Chlorogenic acid gives a bright yellow color, changing to bright carmine on addition of sodium hydroxide in excess; when stabilized with urea the reaction in delicacy is comparable with that of caffeic acid and serves in a study of storage changes in raw coffee.

Carbohydrates.—Spencer⁶ isolated *sucrose* in crystalline form and demonstrated that it is the principal soluble carbohydrate present. *Dextrin* in small amount was reported by the earlier investigators.

¹ Z. Unters. Lebensm. 1933, **66**, 200.

² Z. Unters. Lebensm. 1936, **71**, 217, 393.

³ Arch. Pharm. 1909, **247**, 184.

⁴ Rec. trav. chim. 1912, **31**, 281.

⁵ Chem. Ztg. 1932, **56**, 991.

⁶ U. S. Dept. Agr., Div. Chem. 1892, Bul. **13**, 906.

Reducing sugars are present only in small amount and *starch* is absent, the apparent amounts found by Lythgoe doubtless being due to errors of the method.

The reserve carbohydrate of the seed is chiefly in the thickened cell walls consisting partly of *cellulose* and partly, as shown by Schulze and his students, of *pentosans* and *hemicelluloses*. Warnier¹ found about 5 per cent of pentosans in raw and about half as much in roasted coffee. These amounts added to those for sugar and caffetan- nic acid found by other authors leave a large amount of nitrogen- free extract unaccounted for. Maxwell, as given in notes communi- cated to Spencer,¹ prepared by hydrolysis a considerable amount of *galactose* in crystalline form, thus showing the presence in the bean of the mother substance *galactan*. Reiss² claimed to have isolated man- nose resulting from the hydrolysis of *mannan*, but Spencer failed to corroborate his claim.

Colors.—Angelo³ discusses the presence in unroasted coffee beans of *chlorophyl*, *carotenoids*, *anthocyanins*, and *leucophyl*.

Enzymes.—In a water extract of raw coffee beans, Helferich and Vorsatz⁴ obtained reactions indicating the presence of α -*d*-mannosi- dase, α -*d*-galactosidase, and β -*d*-galactosidase.

Mineral Constituents.—Analyses by Spencer⁵ of the carbon di- oxide-free ash of four of the most common varieties of coffee sold in the United States follow:

COMPOSITION OF COFFEE ASH (SPENCER)

	K ₂ O	Na ₂ O	CaO	MgO	Fe ₂ O ₃	P ₂ O ₅	SO ₃	SiO ₂	Cl	Sand
	%	%	%	%	%	%	%	%	%	%
Mocha.....	59.84	0.48	7.18	10.68	0.89	12.93	4.43	0.88	1.25	1.44
Maracaibo.....	61.82	0.44	5.06	11.30	0.89	13.20	5.10	0.88	0.59	0.72
Java.....	62.08	4.84	11.35	1.16	14.09	4.10	0.91	0.73	0.74
Rio.....	63.60	0.17	4.94	10.60	1.77	11.53	4.88	0.69	0.48	1.34

Minor Mineral Constituents. *Iron.*—Bean 61.6 to 70.2, aver. 66.6; extract (100 grams) 7.9 to 11.3, aver. 9.1 mg. per kilo (Toscani and Reznikoff).⁶

¹ Loc. cit.
² Ber. 1889, 22, 609.
³ Rev. brasil. chim. (São Paulo) 1937, 4, 368.
⁴ Z. physiol. Chem. 1935, 237, 254.
⁵ U. S. Dept. Agr., Div. Chem. 1892, Bul. 13, 904.
⁶ J. Nutrition 1934, 7, 79.

Aluminum.—Bean 46.2 mg. per kilo, dry basis (Bertrand and Lévy).¹

Copper.—Roasted beans 12 to 24 mg. per kilo; caffeine-free coffee 12 to 43 mg. per kilo (Streuli and Bürgin).²

Iodine.—Unroasted 102, roasted 86 γ per kilo, dry basis; 10 per cent water extract (100 grams roasted coffee) 31, extracted coffee 49 γ per kilo (Mayrhofer, Schneider, and Wasitzky).³

Fluorine.—Unroasted 250, roasted 240 γ per kilo, dry basis; 10 per cent water extract (100 grams roasted coffee) 180, extracted coffee 50 γ per kilo (Mayrhofer, Schneider, and Wasitzky).³

Boron.—Partridge ⁴ in all of 31 samples of coffee from six countries secured positive reactions for boron with turmeric. Dodd ⁵ found boron equivalent to about 0.01 per cent of H₃BO₃.

¹ Compt. rend. 1931, **192**, 525.

² Z. Unters. Lebensm. 1936, **72**, 531.

³ Biochem. Z. 1932, **251**, 70.

⁴ Analyst 1927, **52**, 401.

⁵ Ibid. p. 459.

SEEDS OF THE PEA FAMILY

(*Leguminosæ*)

A NUMBER of common leguminous seeds, such as peas, chick peas, and lupines, described in Volume II, after roasting and mixing with chicory, have found favor as alkaloid-free substitutes for coffee. The species described below are known chiefly as coffee substitutes.

COFFEE CASSIA

Cassia occidentalis L. = *C. affinis* Benth.

Fr. Herbe puante. Port. Fedegoso. Ger. Mogdadkaffee.

In many tropical regions this plant grows wild. The seeds are used as a coffee substitute in Brazil, the West Indies, and Africa and have been imported into Europe for the same purpose. The writers have knowledge of a shipment of the seeds into the United States, but have never found it in coffee or coffee substitutes on sale. The root and leaves have been used as drugs.

MACROSCOPIC STRUCTURE.—The *flower* has five unequal sepals and petals. The *pod* is cylindrical or slightly flattened. It contains numerous flattened pear-shaped, dull gray-brown *seeds* (Fig. 27) up to 5 mm. long and 4 mm. wide, with hilum reduced to a mere dot. On each side, either central or eccentric, is an oval patch about half the length of the seed, differing in the character of the surface from that of the rest of the seed. Except for this patch, the surface often has a crackled appearance as if an enamel were flaking off. Cross sections show that the narrow flattened orange cotyledons extend nearly from edge to edge, flanked on both sides by the glassy white endosperm. The radicle is located in the constricted end.

MICROSCOPIC STRUCTURE.—Moeller¹ and Vogl² studied some of the tissues, dwelling on the curious palisade cells and the horny endosperm. Neither author, however, shows the differentiation of

¹ Mikros. Nahr.-Genussm., Berlin, 1905, p. 281.

² Wicht. Nahr.-Genussm., Berlin, 1899, p. 331.

the spermoderm "parenchyma" with three tissues, the presence of a perisperm, and the inner endosperm of thin-walled cells.

Spermoderm (Fig. 28, *S*).—Five layers may be found on careful study, all with brown contents: (1) *palisade cells* (*pal*) up to 85μ high and 7μ wide, with light line (*l*) on the patches up to 35μ , elsewhere up to 15μ , from the flat outer ends, and bulbous swelling of the lumen about 20μ from the inner end as well as at the inner end; (2) *subepiderm* (*sub*) of spool-shaped cells up to 25μ high and about the same breadth with thickened radial walls but without ribs; (3) *parenchyma* (*p*¹) with medium thick walls; (4) *funnel cells* (*fl*); and (5) *inner epiderm* (*br*), structureless in cross section but distinctly cellular in surface view.

Over the surface of the seed, except on the dull patches of the two sides, the outer portion of the *palisade cells* readily scales off at the



FIG. 27.

FIG. 27.—Coffee Cassia. Seed. $\times 1$. (A.L.W.)

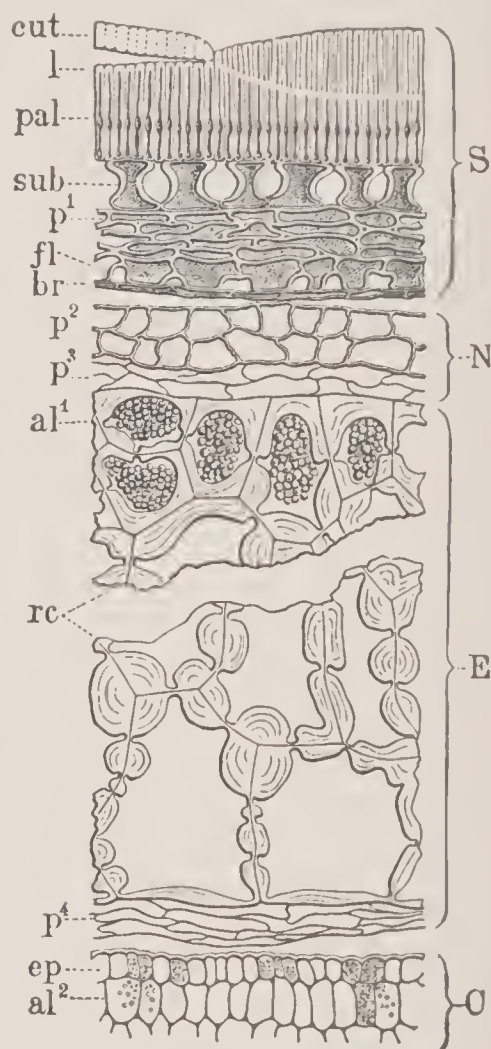


FIG. 28.

FIG. 28.—Coffee Cassia. Seed in cross section through edge of dull patch. *S* spermoderm: *pal* palisade cells with *cut* cuticle scaling off and *l* light line; *sub* subepiderm; *p*¹ parenchyma; *fl* funnel cells; *br* brown inner epiderm. *N* perisperm: *p*² outer, *p*³ inner parenchyma. *E* endosperm: *al*¹ aleurone cells; *rc* thick-walled cells; *p*⁴ compressed cells: *C* cotyledon: *ep* outer epiderm; *al*² aleurone grains of mesophyl. $\times 160$. (K.B.W.)

light line, especially on soaking in water. This outer portion Vogl calls the "cuticular layer" but distinctly states that the palisade cells have a thin (true) cuticle. Beneath the double layer of palisade cells at the hilum the spongy parenchyma is very thick-walled with brown

contents throughout, but in the outer portion the cells and lumen are so reduced in size as to appear colorless. In this region the funnel cells increase somewhat in size and lose their characteristic form.

Perisperm (Fig. 28, *N*).—Two distinct colorless layers, each commonly two cells thick, are evident: the *outer layer* (p^2) with medium thick walls, the *inner layer* (p^3) with exceptionally thin walls.

Endosperm (Fig. 28, *E*).—As in the carob, the *outer endosperm* (rc) has walls greatly thickened with reserve carbohydrate swelling with water; the *inner endosperm* (p^4) has exceedingly thin walls. Distinct aleurone grains (al^1) up to 8μ are present in the single or sometimes double, relatively small peripheral cells, but are not evident in the larger cells further inward or in the inner thin-walled cells.

Embryo.—Cross sections of the *cotyledons* (Fig. 28, *C*) show that the cells are thin-walled throughout, becoming pink on warming with sodium hydroxide, owing probably to color dissolved from the brown spermoderm. Well-marked palisade cells underlie the inner epiderm, while those beneath the outer epiderm, although somewhat radially elongated, are not deserving of that designation. Small aleurone grains (al^2) and fat are the visible contents.

CHIEF STRUCTURAL CHARACTERS.—Seed flattened, pear-shaped 5 mm., brown, with patches on sides. Cotyledons flattened, orange, flanked by white bulky endosperm.

Palisade cells up to 85μ high and 7μ broad with two bulbs in lumen and light line 15 to 35μ from flat upper end; subepiderm spool-shaped, up to 25μ high and broad, without ribs; funnel cells and brown inner epiderm present; perisperm of two distinct colorless layers; endosperm of outer aleurone cells and inner cells with reserve carbohydrate in the walls; embryo tissues thin walled.

CHEMICAL COMPOSITION.—The following analysis is by Moeller¹:

COMPOSITION OF COFFEE CASSIA (MOELLER)

Water	Protein	Fat	Mucilage	Tannin	Other N-f. ext.	Fiber	Ash
% 11.09	% 15.13	% 2.55	% 36.60	% 5.23	% 3.86	% 21.21	% 4.33

¹ Dinglers polytech. J., 237, 61, 84.

Oil.—Steger and Van Loon ¹ obtained by extraction of the kernels a yield of 9.2 per cent of oil having the following values: refractive index at 15° C. 1.4770, saponification number 178.7, iodine number (Wijs) 113.9, Reichert-Meissl number 0.5, acid number 10.2, and thiocyanate number 78.2. It contained saturated acids 19.7, oleic acid 30.7, linolic acid 31.4, linolenic acid 6.3, volatile 0.7, glycerol radical 3.8, and unsaponifiable matter 7.4 per cent.

¹ Rec. trav. chim. 1934, **53**, 28.

ROOTS OF THE COMPOSITE FAMILY

(*Compositæ*)

CHICORY root, much used in coffee, and dandelion root, an occasional adulterant, are products of plants of this family.

CHICORY ROOT

Cichorium Intybus L.

Fr. Racine de chicorée. Sp. Achicoria. It. Cicoria.
Ger. Cichorienwurzel.

As a weed chicory has become cosmopolitan, but its original home appears to be a wide region in Europe, Asia, and Africa. In the wild state the root is narrow and woody; by breeding, varieties with a fleshy root have been developed as well as others described under Leaf Vegetables in Volume II.

Chicory root is best known dried, ground, and roasted as an admixture to coffee. Whether thus used it should be regarded as an adulterant or an improver depends on circumstances. As it is much cheaper than coffee, its presence unknown to the consumer is naturally a fraud; on the other hand many consumers demand chicory in coffee, and in certain sections (as for example in New Orleans) its use is almost universal.

As a root vegetable chicory is not without merit if care is taken in selecting a variety without a strong bitter taste and the roots are eaten while young and tender.

MACROSCOPIC STRUCTURE.—Varieties such as Magdeburg produce long tap roots 4 cm. or more in diameter, light brown on the surface, resembling parsnips in shape. If the soil is not deeply tilled the root splits up into branches. Numerous leaves spring from the crown. When the fresh root is cut transversely its cortex and medullary rays are white, the phloem gray, and the xylem yellow.

MICROSCOPIC STRUCTURE (Figs. 29 and 30.)—Chicory is described in practically all works on the histology of foods and some

on the histology of drugs. The following description applies, except where otherwise stated, to the fleshy cultivated root.

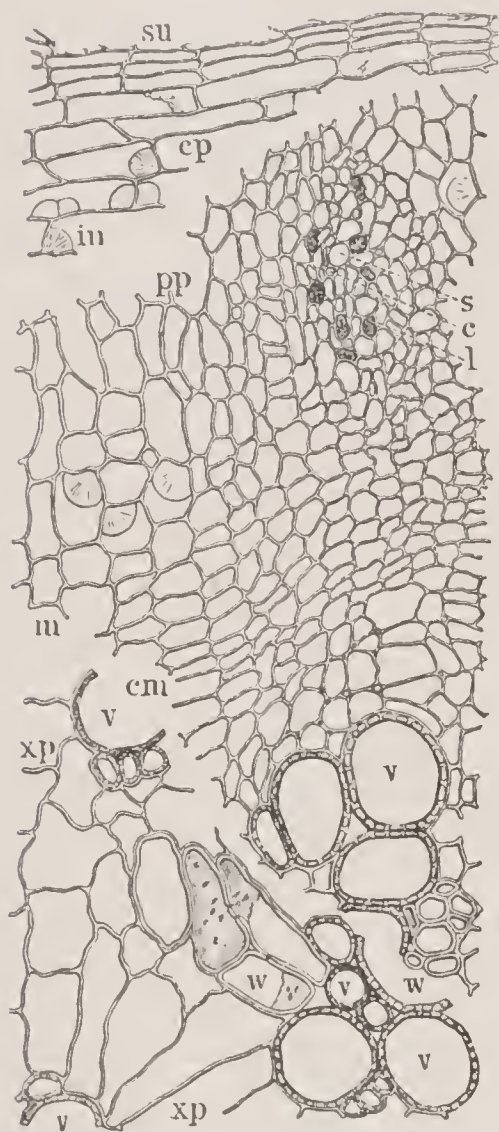


FIG. 29.—Chicory Root. Cross sections through outer, middle (cambium), and central regions. *su* cork; *cp* cortex parenchyma; *in* inulin sphæro-crystals as seen in alcohol material; *m* medullary ray; *pp* phloem parenchyma; *s* sieve tube; *c* companion cell; *l* latex tube; *cm* cambium layer; *v* vessels; *w* wood fibers and cells; *xp* xylem parenchyma. $\times 160$. (A.L.W.)

cells in sections soaked for a time in alcohol.

Sieve tubes (*s*) are readily found in both cross and radial-longi-

Cork (*su*).—The cells in cross and longitudinal sections show the typical arrangement side by side in radial rows. In surface view they are more or less rectangular and transversely elongated.

Cortex (*cp*).—Like the cortical cells of salsify the cells as seen in cross section are transversely elongated, larger than the cork cells, and in longitudinal section are rounded, isodiametric, thus forming intercellular spaces. In full-grown roots an endoderm is not evident even on staining with safranin. Inulin is present as noted under phloem.

Phloem.—The *phloem parenchyma* (*p*, *pp*) consists of thin-walled cells which in cross section are nearly isodiametric, varying in size, and in longitudinal section vary from nearly square in the outer phloem to longitudinally elongated in the inner phloem, the arrangement being side by side in radial rows.

The *medullary rays* (*m*) are one to four cells broad, but are not well differentiated, although the cells may usually be distinguished from the phloem parenchyma by their radial elongation and in longitudinal section by their muriform arrangement.

Inulin (*in*) is the chief cell contents of both phloem parenchyma and medullary rays. It forms an abundance of sphæro-crystals about the angles of the

tudinal sections because of the peculiar refraction of the sieve plates. Accompanying the sieve tubes are *companion cells* (*c*) distinguished by their narrow breadth.

Latex tubes (*l*), the characteristic tissue element of composite roots, form a branching and anastomosing system, some of the branches forming blind ends. The latex contains minute granules, giving the tubes an appearance differing from that of the other elements. The latex tubes of one phloem ray are not, as in the dandelion, connected with those of adjoining rays, and the phloem groups of sieve tubes, companion cells, and latex tubes do not form concentric circles about the root. Phloem tissues of the wild root do not

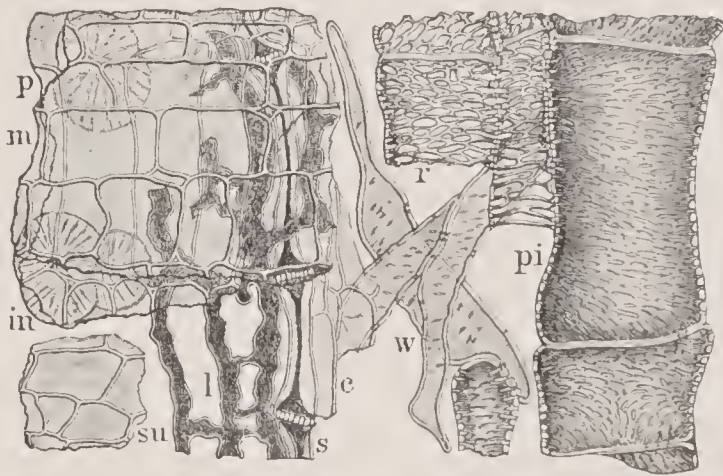


FIG. 30.—Chicory Root. *su* cork in tangential section. Longitudinal radial section of alcohol material: *p* phloem parenchyma with *in* inulin sphæro-crystals; *m* medullary ray; *s* sieve tube; *c* companion cell; *l* latex system. Macerated material: *r* reticulated vessels; *pi* pitted vessels; *w* wood fibers and cells. $\times 160$. (A.L.W.)

differ greatly from those of the cultivated varieties, although the tendency is toward thicker walls.

Cambium (*cm*).—Not conspicuous.

Xylem.—It is in the xylem tissues that the effects of breeding are noticeable. In the cultivated root the *xylem parenchyma* (*xp*) and *medullary rays* are thin-walled and in other respects much like the phloem parenchyma and medullary rays; in the wild root they have thick, porous, sclerenchymatized walls and to a considerable extent are replaced by numerous *libriform fibers* of grotesque form with diagonal pits.

Libriform fibers (*w*) also occur in the cultivated root, especially toward the top, being most abundant in the old roots.

The cells of the *medullary rays* are not so likely to be thick-walled

in wild roots as the xylem parenchyma, hence are often very clearly distinguished.

Breeding does not appear to have materially changed the *vessels* (*v*, *r*, *pi*) which in both cultivated and wild roots reach a maximum breadth of about 115μ . These, as well as the libriform cells, may best be studied after maceration by boiling with hydrochloric acid. The joints of the vessels may be short, the breadth exceeding the length, or long and the pits may be large, forming reticulations (*r*), or small, more or less elongated, the elongation being transverse or in curves with a corner as center (*pi*). Vessels often occur end to end with libriform cells.

In the center of the root the primary group of vessels forms centers for radiating wood parenchyma cells, sometimes interspersed with libriform cells.

CHIEF STRUCTURAL CHARACTERS.—Root light brown, tapering, up to 4 cm. thick or over; cortex and medullary rays white; phloem gray; xylem yellow.

Cork cells rectangular, transversely elongated. Cortex cells similar but larger. Phloem parenchyma longitudinally elongated, rectangular, in radial rows. Cells of medullary rays rectangular, radially elongated, in radial rows. Inulin abundant. Latex tubes branching and anastomosing, accompanying sieve tubes. Vessels up to 115μ with narrow or broad, rather short pits; xylem parenchyma accompanied by libriform fibers.

CHEMICAL COMPOSITION.—Tabulated on p. 171 are analyses by Wolff¹ showing the composition of the chicory root both roasted and unroasted. The analysis of the unroasted sample on the fresh basis has also been calculated to the water basis of the average analysis of the commercially roasted root, thus making it clear that the inulin is largely converted by the roasting process into caramel, sugars, and other water-soluble forms.

Results by Bernard Dyer² are in accord with those of Wolff so far as the medium-roasted product is concerned. When strongly roasted, the insoluble solids are about doubled owing to the formation of charcoal.

LaWall and Forman³ find that an important distinction of coffee from mixtures of coffee and chicory is the percentage of reducing sugars in the water extract. Coffee extract contains only 1.92 to 2.64

¹ Ann. chim. anal. 1899, 4, 157.

² Analyst 1898, 23, 226.

³ Am. J. Pharm. 1913, 85, 535.

COMPOSITION OF RAW AND ROASTED CHICORY ROOT (WOLFF)

	Water	Pro- tein	Fat	Sugar	Cara- mel	Inulin	N-f. ext.	Fiber	Ash	Sol- uble solids
	%	%	%	%	%	%	%	%	%	%
Unroasted.....	79.20	1.15	0.11	0.60	14.00*	16.80	1.29	1.11
Roasted by analyst	16.00	6.15	1.70	14.40	9.00	9.60	64.20	9.10	2.75	61.00
Roasted by trade:										
Min.....	9.20	5.50	1.70	7.50	11.60	4.00	60.70	6.50	3.70	54.30
Max.....	14.50	6.60	2.70	14.20	15.60	9.60	66.40	13.20	8.50	65.90
Aver.....	12.34	6.10	2.33	11.10	13.40	5.90	63.82	9.24	5.80	60.12
Unroasted†.....	12.34	4.85	0.46	2.53	59.00	70.80	5.43	4.68

* Average. † First analysis calculated to 12.34% water content.

COMPOSITION OF ROASTED CHICORY ROOT (DYER)

	Protein	Fat	Total ash	Soluble ash	Sand	Soluble solids	Insoluble solids
	%	%	%	%	%	%	%
Medium roasted..	9.56	2.57	4.63	2.50	0.70	77.6	22.4
Heavy roasted...	10.64	2.43	4.70	2.99	0.30	49.7	50.3
Powder (9):							
Min.....	7.69	1.90	5.13	1.60	0.77	62.2	21.5
Max.....	9.50	3.87	8.23	3.30	3.97	78.5	37.8

aver. **2.29** per cent of reducing sugars, whereas, 2 samples of chicory extract contained 27.67 and 25.20 per cent and an extract of a mixture of 95 per cent coffee and 5 per cent chicory contained 4.62 per cent. This principle applied to the infusion brings out equally strong distinctions.

Traub, Thor, Zeleny, and Willaman,¹ who have suggested the feasibility of manufacturing fructose from inulin-containing roots and tubers, give the following analyses of roots grown in Minnesota. It will be noted that the percentages of fructose, not of inulin from which the fructose is formed by hydrolysis, also glucose which corresponds to reducing sugars, are given.

CONSTITUENTS. Oil.—As a result of roasting, a tarry oil is formed. Grafe² states that this oil is analogous to coffee oil and that

¹ J. Agr. Res. 1929, 39, 551.

² Biochem. Z. 1915, 68, 1.

COMPOSITION OF FRESH CHICORY ROOT (TRAUB ET AL.)

Variety	Date	Water	Protein	Total sugar	Glucose	Fructose	Ash
		%	%	%	%	%	%
Large-rooted Magdeburg...	Sep. 15	81.7	1.25	13.66	3.53	10.13	0.72
" " " ...	Oct. 14	79.4	1.37	16.57	5.99	10.58	0.73
Westland's Strain.....	Sep. 15	80.6	1.20	14.15	3.47	10.68	0.79
" "	Oct. 14	77.6	1.62	17.42	6.63	10.79	0.71

it contains *acetic acid* 63.5, *valeric acid* 5.4, *acrolein* 2.5, *furfural* 2.3, and *furfuryl alcohol* 23.5 per cent.

Organic Acids.—Arbenz¹ found 0.07 per cent of *oxalic acid* in roasted chicory.

Inulin.—It has long been known that inulin, which does not reduce copper and polarizes to the left (about -18) on acid hydrolysis, passes into *d*-fructose that reduces copper to nearly the same degree as *d*-glucose and polarizes -92 . Experiments by Wolff and Geslin² show that during storage the inulin of chicory is also hydrolyzed to fructose by a diastase which appears to be identical with the sucrase of yeast, with the formation of a series of intermediate products which they call inulides. The changes are analogous to those which take place when starch is hydrolyzed by diastase through a series of dextrans into maltose and finally by acid into glucose. In their further studies the authors found that three groups of inulides are formed, differing in that each group is fermented by a different yeast. They distinguish between inulides and levulosans, a term used in a broader sense for carbohydrates hydrolyzing to fructose (levulose). They also state that the amount of sucrose present is small.

An enzyme, *inulo-coagulase*, found by Wolff³ in the chicory root, coagulates inulin of the juice. By boiling for a few seconds the enzyme is destroyed.

Bitter Principle.—Grafe⁴ postulated that the bitter principle is a glucoside of levulose and protocathechuic aldehyde derived from inulin. Twenty-one years later⁵ he showed that it consists of 1 part

¹ Mitt. Lebensm. Hyg. 1917, 8, 98.

² Compt. rend. 1917, 165, 651: 1918, 166, 428.

³ Ibid. 1916, 162, 514.

⁴ Loc. cit.

⁵ Beitr. Biol. Pflanzen 1936, 24, 138.

of protocatechualdehyde and 3 of inulin. It occurs in the seed, but, although only the inulin remains immediately after sprouting, the aldehyde reappears in a few days, corresponding to the simplest molecular formula $C_{24}H_{32}O_{16}$.

Enzymes.—See Inulin.

Mineral Constituents.—The following analysis is given by König¹:

Ash	K ₂ O	Na ₂ O	CaO	MgO	Fe ₂ O ₃	P ₂ O ₅	SO ₃	SiO ₂	Cl
%	%	%	%	%	%	%	%	%	%
0.85	38.30	15.68	7.02	4.69	2.51	12.49	7.93	0.91	8.04

Minor Mineral Constituents. *Arsenic.*—Root 0.1 mg. per kilo, fresh basis (Jadin and Astruc).²

DANDELION ROOT

Taraxacum officinale Weber = *T. Dens-leonis* Desf.

Fr. Dent-de-lion. Sp. Diente de león. It. Macerone.
Ger. Löwenzahn.

The leaves of the common dandelion are valuable as greens, but the root is not considered edible although used in medicine. However, it is said to be used as an adulterant of chicory, and for this reason the microscopic differences in the two roots have been described by authors on food histology.

MACROSCOPIC STRUCTURE.—Cross sections show that the phloem has a concentric structure, the latex exuding in the fresh root making this structure particularly striking, and the central wood tissue (xylem) is relatively narrow, forming only one-fifth of the thickness of the root.

MICROSCOPIC STRUCTURE.—The concentric structure, visible to the naked eye, is due to groups of *sieve tubes* and *latex tubes* arranged in circles. This is a marked distinction from chicory in which the groups are stretched along the phloem rays without marked interruption.

Numerous *vessels* make up a greater relative bulk in the xylem than they do in chicory, even the wild form. In longitudinal section or

¹ Chem. mensh. Nahr.-Genussm., Berlin, 1920, 2, 874.

² Compt. rend. 1912, 155, 291.

the macerated material they are distinguished by the longer pits which in the large vessels run nearly or quite across the entire breadth.

The *xylem parenchyma* has somewhat thickened walls as in chicory.

CHIEF STRUCTURAL CHARACTERS.—Phloem shows concentric rings due to groups of sieve tubes and latex tubes. Vessels with long pits (rather short in chicory).

CHEMICAL COMPOSITION.—Dragendorff¹ demonstrated that the *inulin* largely disappears during the Winter, roots gathered in October containing 24 per cent and those gathered in March only 1.74 per cent. The roots in the latter case, however, contain 17 per cent of non-crystallizable sugars and 18.7 per cent of *laevulin*. All Dragendorff's results appear to be on the air-dry basis.

Our knowledge of the bitter principle is based chiefly on results of early work which needs revision.

¹ Materialien zu einer Monographie des Inulins, St. Petersburg, 1870, p. 135.

PART III
SPICES AND EXTRACTS

PART III

SPICES AND EXTRACTS

INTRODUCTION

ALTHOUGH flavor is an important factor in making food more enjoyable, it is no more a mark of nutritive value than color in fabrics is a measure of durability. As has been emphasized by one of us elsewhere, practically all the members of the three great groups of nutrients, proteins, fat, and carbohydrates, excepting the sweet carbohydrates, are tasteless or nearly so, the agreeable flavors of foods containing them being due to minor constituents present naturally or added during preparation. To the latter class belong spices, pot herbs, flavoring extracts, and a few unclassified substances, none of which serves directly in any appreciable degree for fuel or repair of animal tissues.

The number of food adjuncts that contribute flavor and zest to our diet is large and that of the valuable chemical principles is still larger, notwithstanding the frequent occurrence of the same principle in several different products.

Sugar and salt, being true foods, are not here considered.

Although widely different chemically from the spices, vinegar is distinctly a flavor. As is true of the spices, the chief constituent—in this case acetic acid—is not the only valuable constituent, since certain minor constituents of cider, wine, and malt vinegars combine to give each a distinctive flavor which differs materially from that of spirit vinegar or dilute acetic acid.

In the strict sense spices include only such pungent leaves, flowers, seeds, bark, and rhizomes as are suited either whole or ground for culinary use. A few other products, such as vanilla beans, tonka beans, and rinds of citrous fruits, may be classed with spices under the broader head of food flavors.

The flavoring principles of the natural products are commercially separated from the inert portion by distillation (numerous volatile

oils), pressure (citrous oils), or dissolving in alcohol (vanilla and tonka extracts), for use in foods either directly or after dilution with alcohol to standard strength, forming the so-called flavoring extracts.

CHEMICAL CONSTITUENTS OF SPICES.—For a better understanding of the tables on composition of the spices, certain features of the analytical methods need explanation.

Although spices have practically no food value, the general plan of proximate analysis designed primarily for cereals and other true foods is suited also for spices; the presence of *volatile oil*, however, is a disturbing element that necessitates modification of the methods for determination of *water* and *fat* (fixed oil).

Following the usual method of drying at the temperature of boiling water for the determination of water, part of the volatile oil passes off with the moisture and all of it may be removed if the temperature is somewhat raised and the time of heating is extended, thus obtaining from the loss the percentage of the two together.

Extraction with ether in a continuous-flow apparatus removes volatile oil as well as fat (fixed oil) and other non-volatile ether-soluble substances, but heating the extract to drive off the last traces of ether would also cause loss of a portion of the volatile oil. To prevent this loss, the ether is allowed to evaporate in an open dish at room temperature and the final drying carried out in a desiccator. After the joint extract is weighed, the volatile oil is removed by heating and the fixed oil weighed, thus permitting the calculation of the percentage of both oils. The loss of oil on drying the spice at 100 to 110° C. less that of the joint extract at the same temperature represents water. The method outlined, although far from perfect, answers for most purposes. The volatile oil may also be determined by distillation with steam, separation of the oil layer from the watery portion of the distillate, and determination of its volume or weight, the process being in miniature substantially that followed in the commercial manufacture of essential oils.

Protein (nitrogen \times 6.25, except in special cases such as the presence of *piperine* and other alkaloids in pepper), *sugar*, *starch*, *fiber*, and *ash constituents* are comparable with the same constituents in cereals, oil seeds, and other foods and are determined by the same methods.

Fixed Oil.—In some seeds, notably those of the mustard group, the fixed oil is bland and distinctly fatty; in seeds rich in essential oil, it is more or less resinous. It may be pungent; for example, the fixed oil of black and white pepper consists largely of piperine, while that of red

pepper contains the intensely biting principle capsaicin, and that of ginger contains the pungent substance zingerone.

Physical and Chemical Values.—See Part II, Volume I.

Volatile Oil.¹—Francesconi² has studied the origin of volatile oil and the transition of one constituent to another.

Physical and Chemical Values.—Although volatile oils, like fixed oils, are insoluble in water, but soluble in fat solvents, they differ from most fixed oils in being also soluble in alcohol to a greater or lesser extent according to the dilution and also in being vaporized with steam. They further differ from fixed oils in that most of them, examined in a 1-decimeter tube of the polariscope, are optically active, the degree of rotation being given as *optical rotation* or α_D and not as specific rotation $[\alpha]_D$ which requires useless calculation. Improper use of the brackets about the α has led to much misunderstanding. The temperature of observation, when determined, is expressed as a figure over the D, thus $^{20}_D$. Chugaev and Chesno³ give the optical rotation for different wave lengths and the dispersion coefficient of a large number of essential oils.

In judging both classes of oils, the *specific gravity* at 15° C. and the *refractive index* at 20° C, are useful values. Utz⁴ and Parry⁵ give tables showing the refractive indexes of numerous oils.

Of the chemical values, the *iodine number*, which is highly significant for fixed oils, as emphasized by Parry is of little or no use as a characteristic of volatile oils, but Winkler⁶ claims that the *iodine-bromine number* is significant for both fixed and volatile oils. The *acid number* (milligrams of potassium hydroxide per gram of oil) is commonly determined in both oils. The *saponification number* may

¹ The following works treat of the production, chemistry, and analysis of essential oils. Allen's Commercial Organic Analysis, Philadelphia, 5th Ed., Vol. IV (Essential Oils: Special Characters by Nelson and Russell; Constituents, General Characters, and Analysis by Parry) 1924; Finnemore: The Essential Oils, London, 1926; Gildemeister and Hoffman: Die ätherischen Öle Leipzig, 2nd English Ed. (two vols.) 1915; 3rd German Ed. Vol. I, 1928, Vol. II, 1929, Vol. III, 1931; Parry: Chemistry of Essential Oils and Artificial Perfumes, London, 3rd Ed. Vol. II (Constituents; Analysis) 1919; 4th Ed. Vol. 1 (Monographs) 1921. The Semi-annual and Annual Reports of Schimmel & Co. published since 1890 in both German and English, and the Roure-Bertrand fils Sci. Ind. Bul. contain much original matter.

² Riv. ital. ess. profum. 1928, 10, 33, 78.

³ Trans. Sci. Chem. Pharm. Inst. (Moscow) 1928, No. 19, 181.

⁴ Apoth. Ztg. 1901, p. 742.

⁵ Chem. Drug. 1910, 77, 314; Allen's Com'l Org. Anal., Philadelphia, 4th Ed. 1911, 4, 244 and 1917, 9, 339, also 5th Ed.

⁶ Pharm. Zentralh. 1927, 68, 433.

be determined in volatile oils, but it is now customary to carry out the saponification on the neutralized portion used for the determination of the acid number, the value in terms of milligrams of potassium hydroxide per gram of oil being designated *ester number*, since it represents the alcohols combined as esters displaced by the alkali. The *ester number after acetylation* (esterification), corresponding to the *acetyl number* of fixed oils, is a measure of the total alcohols including the *combined alcohols* of the esters and the *free alcohols* which, following the conventional method, by boiling with acetic anhydride in the presence of anhydrous sodium acetate are converted into acetic esters (acetates). Although the cumbersome term ester number after acetylation is now often employed, the authors of this work cling to the old term acetyl number because of its brevity and long use in the analysis of fatty oils. A new term "alcohol number" would have the advantage of suggesting that the number is a measure of total alcohols.

When the ester or esters of a certain alcohol are known to predominate, the percentage of the acetate (acetic ester) of that alcohol may be calculated from the ester number. Again the combined (as esters), free, and total alcohol may be obtained in terms of the predominating alcohol. The reverse calculation may also be made.

In the following formulas *K* is the ester number, *A* the acetyl number, *E* the percentage of acetate (acetic ester), and *C*, *F*, and *T* the percentages of combined, free, and total alcohol respectively:

Terpineol, Geraniol, Linalöl, Borneol
($C_{10}H_{18}O$)

$$E = 0.35K$$

$$C = 0.275K$$

$$T = \frac{7.7A}{28 - 0.021A}$$

$$F = T - C$$

$$K = 2.857E = 3.636C$$

$$A = \frac{28T}{7.7 + 0.021T}$$

Menthol, Citronellol
($C_{10}H_{20}O$)

$$E = 0.3536K$$

$$C = 0.279K$$

$$T = \frac{7.8A}{28 - 0.021A}$$

$$K = 2.828E = 3.584C$$

$$A = \frac{28T}{7.8 + 0.021T}$$

Gildemeister and Hoffmann¹ give calculation tables for alcohols of different molecular weights with columns showing the following equivalents: (1) ester number, (2) percentage of acetate, (3) percentage of alcohol in the acetylated oil, and (4) percentage of alcohol in the original oil corresponding to (3).

¹ Ätherischen Öle, Leipzig, 3 Aufl. 1928, 1.

French oil chemists determine, instead of the usual ester number after acetylation (acetyl number), the *ester number after formylation* (*formyl number*) by a method proposed by Glichitch.¹ In this method the oil is acted on by the aceto-formic anhydride of Behal² prepared by adding 1 part of formic acid to 2 parts of acetic anhydride. The formulas for calculation of T and A, the latter in the present case being the ester number after formylation, differ from those given above in that 0.014 is substituted for 0.021 in the denominators.

The ester number of the hydrogenated and esterified oil is determined by some authors.

Hydrogen Number.—This value, like the iodine number of fatty oils, is a measure of unsaturation. As determined by the method devised by Albright,³ using colloidal palladium as a catalyzer and his special apparatus, it is the number of cubic centimeters of hydrogen at 0° C. and 760 mm. pressure absorbed by 1 gram of the sample during the period of most rapid absorption, when the allyl or propenyl groups are saturated and before the slower reaction involving the second double bond takes place to any great extent.

Constituents.—Like the fatty oils, the volatile oils are mixtures of chemical individuals, one or more of which may be characteristic of a botanical genus or family, as for example limonene of citrous fruits, menthol of labiate leaves, and anethole of umbelliferous seeds. The method of formation and location in the tissues are sometimes correlated with similarity in composition. It should be borne in mind that volatile oils owe their flavor to their volatility, that is they are odorous, and do not contain fixed (non-volatile) substances with a distinct taste such as sugar, salt, tannin, piperine, and capsaicin. With few exceptions the constituents fall into the following eight groups, the structure of typical examples being shown on pp. 184 and 185, and also under Nutmeg.

1. *Terpenes.*—Most of the constituents of the volatile oils are hydrocarbons or related oxygenated substances. In the strict sense only hydrocarbons with the formula $C_{10}H_{16}$ are terpenes; it is convenient, however, to consider that the true terpenes and related oxygenated substances, including alcohols, aldehydes, ketones, and esters, occurring naturally with them form a group analogous to the carotenoids. They are regarded as derivatives of menthane or hexahydrocymene, $C_{10}H_{20}$, which has a ring with no double bonds, whereas

¹ Compt. rend. 1923, 177, 268.

² Bul. soc. chim. 1900, [3], 23, 745.

³ J. Am. Chem. Soc. 1914, 36, 2188.

cymene itself has the typical benzene ring. Examples of monocyclic terpenes are *limonene* and *phellandrene*, and an example of a dicyclic terpene is *pinene*. See formulas, p. 185.

2. *Sesquiterpenes*, $C_{15}H_{24}$, are less important than the true terpenes and not so well understood. Examples are *caryophyllene* of cloves and *zingiberene* of ginger. *Zingiberol* is a sesquiterpene alcohol.

3. *Alcohols*.—Aliphatic alcohols such as methanol and ethanol are minor constituents. Secondary open-chain dihydro alcohols, related to the terpenes, and phenol alcohols are important constituents.

4. *Aldehydes*.—In addition to citral, an aldehyde closely related to the terpenes noted above, various aromatic aldehydes are characteristic constituents of certain volatile oils, notable examples being three oily substances, namely *benzaldehyde* of bitter almond oil, *cinnamal* of cinnamon and cassia oils, and *cuminal* of cumin oil. Two crystalline aldehydes occurring in nature with other odorous substances and synthesized in a state of purity are highly esteemed as flavors or perfumes; these are *vanillin* of the vanilla bean and *heliotropin* of the heliotrope flowers.

5. *Esters*.—Some of these are phenol derivatives as noted above; others are esters of aromatic acids, *methyl salicylate* of wintergreen and birch oils being an example; and still others are compounds of terpene bases and aliphatic acids, *menthyl acetate* of labiate oils being an example.

6. *Phenols and Derivatives*.—This group consists of derivatives of benzene in which two or more of the hydrogen atoms are replaced directly by alkyl (methyl or propyl), allyl, or hydroxy radicals, or else by methoxy radicals forming esters. Examples of the phenols are *thymol* and *carvacrol* of thyme oil; examples of esters are *anethole* and *apiole* of umbelliferous oils and *safrole* of sassafras oil.

7. *Acids*.—Although occurring free only in small amount, a considerable number of organic acids have been isolated from volatile oil. They include members of the fatty acids, both low and high in the series, also acids of the benzene series, notably salicylic acid.

8. *Thiocyanates and Sulphides*.—*Allyl thiocyanate* is the pungent principle of volatile mustard oil. *Allyl sulphide* occurs in oils of the onion group and *dimethyl sulphide* in peppermint oil.

The structural formulas displayed on pp. 184 and 185 show the relationship between the members of the terpene group (hydrocarbons, alcohols, esters, aldehydes, and ketones) and the strictly aromatic compounds with three double bonds in the ring (phenols, phenyl alcohols, phenyl esters, etc.). The arrangement of the symbols

and bonds in the formulas for pinene, borneol, cineol, geraniol, and citral is such as to permit ready comparison with formulas of other substances. Attention is directed to the primary, secondary, and tertiary alcohols, also to the propenyl ($\text{CH} : \text{CH} \cdot \text{CH}_3$) and allyl ($\text{CH}_2 \cdot \text{CH} : \text{CH}_2$) groups in the phenols and derivatives.

Water-Soluble Flavoring Principles.—Certain constituents with marked flavor are fixed solids soluble in water but insoluble in fat solvents. Examples are *sinalbin*, a nitrogen- and sulphur-containing principle of white mustard, various astringent substances notably *tannins*, and *bitter constituents*.

Inert Organic Constituents.—The bulk of the natural products is made up of constituents of no flavoring value. Determination of these constituents, however, is often desirable in examining spices with reference to their grade or purity.

Nitrogenous Constituents.—In most species protein is obtained by multiplying the percentage of nitrogen by 6.25. Allowance must be made, however, for piperine and other ether-soluble substances present in black, white, and long pepper. The mustards contain sulphonyl cyanates and allied compounds, but the nitrogen content of these is small compared with that of the proteins.

Ether Extract is synonymous with fat or oil when applied to mustards and red peppers, which contain neither essential oils nor resins. The ether extract of leaves is rich in chlorophyll. The non-volatile ether extract of most species contains resin as well as fat or oil; that of black, white, and long pepper contains piperine.

Soluble Carbohydrates, including sugars and dextrans, are not abundant in most species.

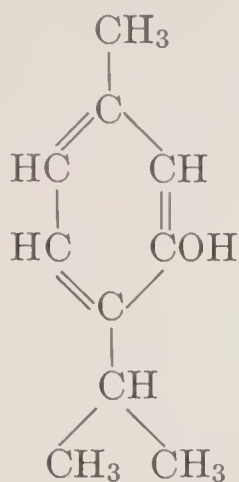
Starch is present in certain seeds (e.g., pepper, allspice, nutmegs), barks (e.g., cinnamon), and rhizomes (e.g., ginger and turmeric). It is accurately determined by the diastase method, and with fair approximation, after washing out the soluble carbohydrates, by direct inversion, provided that fiber is present in small amount.

Cell Wall Material.—Fiber—the term as explained in Volume I is used instead of “crude fiber”—includes cellulose and lignin. Other cell wall constituents are pentosans and pectins.

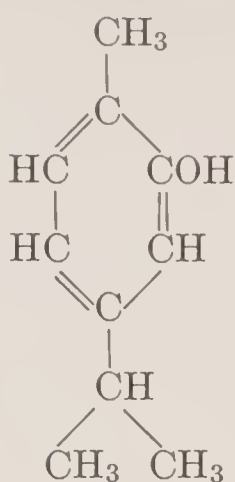
Hanus and Bien,¹ who determined the pentosans in 39 spices, call attention to the association of high fiber and high pentosans. Their results are given under the individual species.

Ash.—Carefully grown, selected, and handled species contain little or no mineral matter other than that normal to the tissues. During

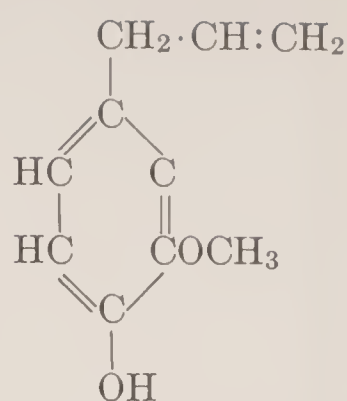
¹ Z. Unters. Nahr.-Genussm. 1906, 12, 395.



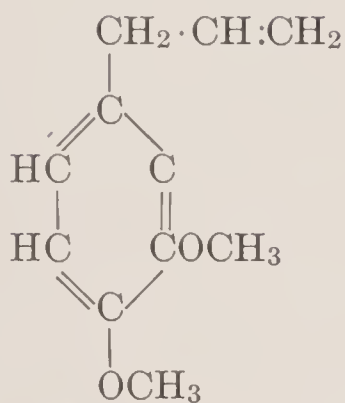
Thymol
(phenol)



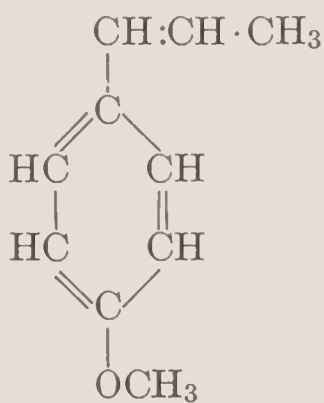
Carvacrol
(phenol)



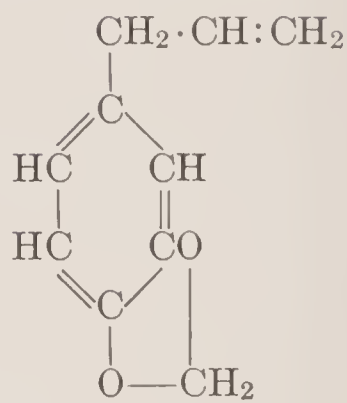
Eugenol
(phenol)



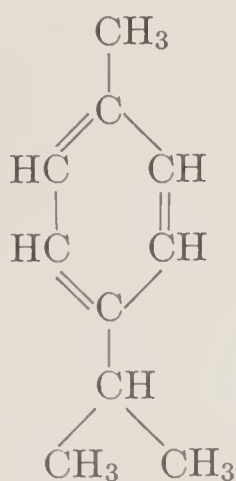
Methyl eugenol
(phenyl ester)



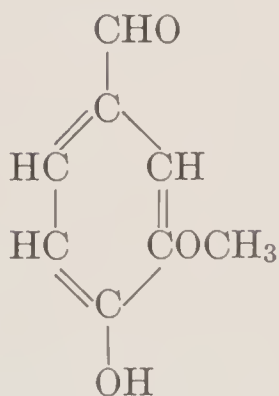
Anethole
(phenyl ester)



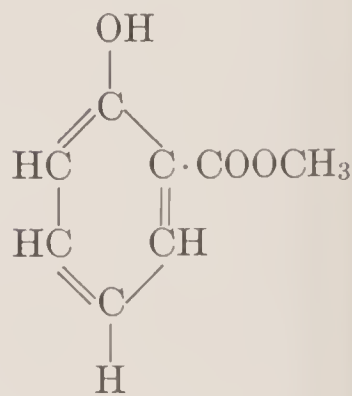
Safrole
(phenyl ester)



Cymene
(aromatic hydrocarbon)

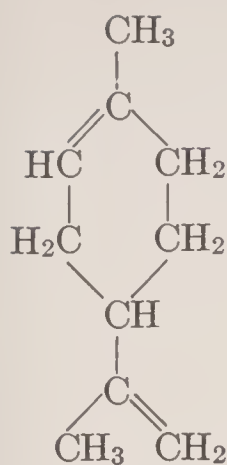


Vanillin
(aromatic aldehyde)

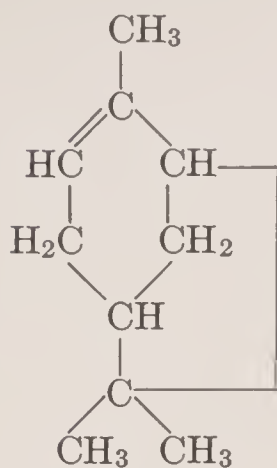


Methyl salicylate
(aromatic ester)

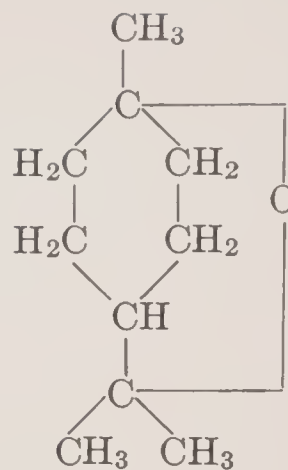
Phenols and related constituents of volatile oils



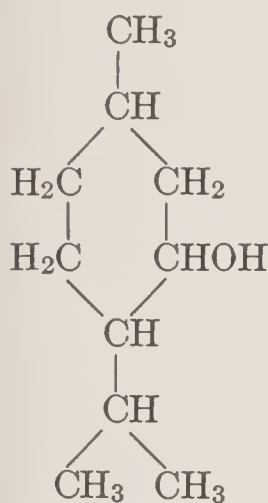
Limonene
(terpene)



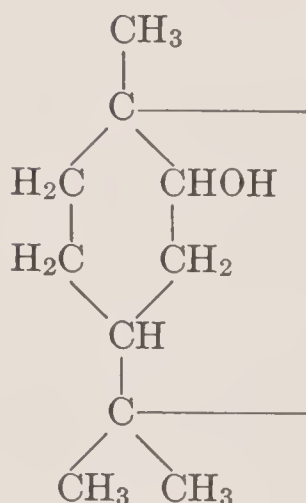
Pinene
(terpene)



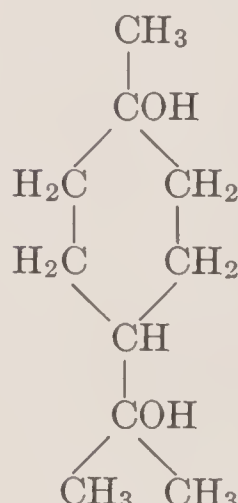
Cineol
(terpene oxide)



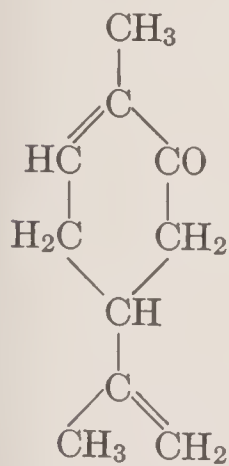
Menthol
(secondary terpene-alcohol)



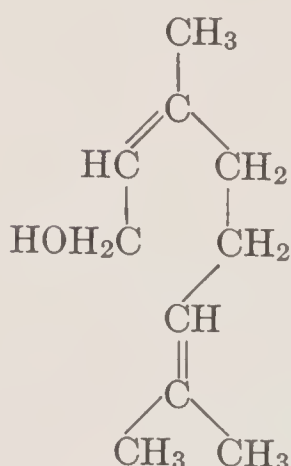
Borneol
(secondary terpene-alcohol)



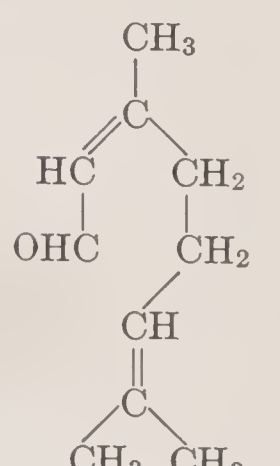
Terpinol
(dihydric tertiary terpene-alcohol)



Carvone
(terpene-ketone)



Geraniol
(open-chain primary alcohol)



Citral
(open-chain aldehyde)

Terpenes and related constituents of volatile oils

certain seasons, however, owing to spattering of the soil or dust clouds, contamination is unavoidable. Since an excessively high percentage of total ash and sand (acid-insoluble ash, ash insoluble in hydrochloric acid) is indicative of inferiority if not willful neglect, determinations of these is a part of the routine examination of both unground and ground spices.

STEM AND LEAF SPICES

UNDER this head are included the leaves or terminal leafy stems of pot herbs and various other plants used directly for seasoning or for the manufacture of volatile oils which as such or in alcoholic solution are valuable for flavoring pastries, confectionery, and beverages. Rhizomes, such as ginger, turmeric, and calamus, being fleshy subterranean stems, are also here included. Barks of woody plants are described in a separate section.

LEAVES OF THE GRASS FAMILY

(*Gramineæ*)

THE leaves of *Anthoxanthum odoratum*, mentioned under Tonka Bean, contain coumarin but are not to our knowledge used for flavoring. Two grasses, namely lemon grass and citronella, yield volatile oils sometimes substituted for lemon oil.

LEMON GRASS

Cymbopogon citratus DC. = *Andropogon citratus* DC.

Fr. Mélisse indienne. Ger. Lemongras.

This species, long grown in the East Indies, has been introduced into the West Indies and tropical South America. The leaves, as well as those of *C. flexuosus*, yield an aromatic oil.

Lemon Grass Oil, as prepared by distillation, is used in perfumery and sometimes is substituted for lemon oil in the manufacture of lemon extract.

Physical and Chemical Values.—Results by numerous authors, notably Schimmel & Co.,¹ Parry,² Umney,³ Kafuku,⁴ Squibbs,⁵

¹ Schimmel & Co. Ber. Oct. 1913, 68; Oct. 1914, Apr. 1915, 28.

² Perf. Ess. Oil Rec. 1913, 4, 40.

³ Ibid. 1913, 4, 3.

⁴ J. Soc. Chem. Ind. (Japan) 1916, 19, 403.

⁵ Seychelles Dept. Agr. Rep. 1933, p. 9.

Holdsworth-Haines¹ and Sergès² appear to warrant the following range:

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Citral	Sol. 70% alcohol
			°	%	vols.
Min.	0.880	1.4820	−4.5	70	1.5
Max.	0.905	1.4885	+3	90	3.0

Analyses of 6 samples of Uganda oil³ made from (1) fresh leaves, (2) shade-dried leaves, (3) rust-free leaves, (4) badly rusted leaves, (5) butts, and (6) very dry leaves gave, respectively: specific gravity at 15.5° C. 0.8834, 0.8805, 0.8831, 0.8812, 0.8825, 0.8756; refractive index at 20° C. 1.4850, 1.4847, 1.4850, 1.4850, 1.4848, 1.4835; optical rotation at 16–17° C. −0.10, −0.09, −0.11, −0.11, −0.30, −0.12°; citral by bisulphate method by volume and by weight 76.5 and 74.2, 74.5 and 73.8, 79.5 and 77.1, 77.5 and 77.1, 75.5 and 75.1, 72.0 and 71.1 per cent respectively.

Constituents.—The oil contains, in addition to *citral* first isolated by Bertram,⁴ small amounts of *n-decylaldehyde* and an isomer of citral.⁵ The citriodor-aldehyde and allolemonal of Stiehl⁶ have been shown⁷ to be identical with citral or mixtures. Barbier and Bouveault⁸ isolated the ketone *methyl heptenone*. Schimmel & Co.⁹ report in the East Indian oil the alcohol *geraniol*, also one believed to be *linalool*, and Elze,¹⁰ *methyl heptenol*, *nerol*, and *farnesol*. According to Stiehl,⁶ the terpene *dipentene* and perhaps *limonene* are present in East Indian oil, and, according to Kafuku,¹¹ the terpene *myrcene* in Formosan oil.

¹ Ibid. p. 23.

² Chim. ind. agr. biol. 1938, **14**, 161.

³ Uganda Protectorate Dept. Agr. Rep. 1934, II, p. 97.

⁴ Schimmel & Co. Ber. Oct. 1888, 17.

⁵ Schimmel & Co. Rep. Oct. 1905, 45.

⁶ J. prakt. Chem. 1898, II, **58**, 51; 1899, **59**, 497.

⁷ Schimmel & Co. Rep. Oct. 1898, 58; Pobner: Ber. 1898, **31**, 3195.

⁸ Compt. rend. 1894, **118**, 983.

⁹ Rep. Oct. 1894, 33; Apr. 1899, 65.

¹⁰ Riechstoff Ind. 1929, **4**, 22.

¹¹ J. Soc. Chem. Ind. (Japan) 1916, **19**, 403; 1917, **20**, 825.

CITRONELLA

Cymbopogon Nardus Rendle = *Andropogon Nardus* L.;
C. Winterianus Jowitt

Fr. Citronelle. Ger. Citronellgras.

The first of the above-named species, known as *lana batu*, yields Ceylon oil; the second, known as *maha pangiri*, yields Java oil. The latter is the more valuable.

Citronella Oil, as distilled from the grass, is a deep yellow liquid well known as a protection against mosquitoes. It serves chiefly as a perfume, but has been used in the preparation of cheap substitutes for lemon extract.

Physical and Chemical Values.—The Ceylon oil has a somewhat higher specific gravity, refraction, and levorotation than that from Singapore and Java. The limits below are sufficiently wide to include the values of all common varieties:

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Sol. 80% alcohol
Min.	0.881	1.463	° −40	vols. 1
Max.	0.925	1.494	0	2

Squibbs¹ in Seychelles oil reports aldehydes (bisulphite method) 9.0 per cent and ester number after acetylation 211.5.

Constituents.—Two isomers, the alcohol *geraniol* and the aldehyde *citronellal* (C₁₀H₁₈O), the latter being the chief odorous constituent, make up the bulk of both Ceylon and Java oils. Samples of the former, analyzed by Schimmel & Co.,² contained geraniol 29.6 to 34.4 per cent and citronellal 6.5 to 11.6 per cent; samples of the latter contained geraniol 26.6 to 45 per cent and citronellal 35 to 46.3 per cent. Gildemeister and Hoffmann³ extend the limits for citronellal to the following: Ceylon oil 5 to 15 per cent, Java oil 25 to 54 per cent.

¹ Seychelles Dept. Agr. Rep. 1933, p. 9.

² Rep. 1912, 43, 44, 45; Apr. 1913.

³ Ätherischen Öle, Leipzig, 3 Aufl. 1929, 2, 335.

Furukawa ¹ found in Ceylon oil 58.6 per cent of acetylatable matter ("total geraniol") and in Java oil 87 to 93.97 per cent.

Several authors ² have identified a considerable number of minor constituents of which the following occur in both commercial oils: *citronellol*, *methyl eugenol*, *dipentene*, *l-limonene*, and certain *sesquiterpenes*. Those reported only in Ceylon oil are *l-borneol*, *farnesol*, *nerol*, *isovaleryl alcohol*, *isovaleryl aldehyde*, *methyl heptenone*, and *camphene*; those peculiar to Java oil are *citral*, *citronelloxide*, *eugenol*, and two alcohols, both $C_{15}H_{26}O$, constituting the bulk of the sesquiterpene fraction of 5 to 10 per cent, one monocyclic, solid (*elenol*), the other bicyclic, liquid (unnamed).

Fugita ³ believes that the progressive decrease in ester value and total alcohol content observed in Java citronella grown in Formosa and the correlated low specific gravity and high levorotation point to the following transformations which may apply also to other oils: citronellal and citronellyl ester to citronellol, then to geraniol, and finally to sesquiterpenes, limonene, and myrcene.

¹ J. Soc. Chem. Ind. (Japan) 1918, **21**, 515.

² Schimmel & Co. Rep. Oct. 1893, 15; Oct. 1898, 11; Oct. 1899, 24; Apr. 1900, 12; Apr. 1902, 21; Apr. 1910, 29; Apr. 1912, 47. Bertram and Walbaum: J. prakt. Chem. 1894, II, **49**, 16. Dupont and Labaune: Roure-Bertrand fils Bul. Apr. 1912, 8. Semmler and Spornitz: Ber. 1913, **46**, 4025. Elze: Chem. Ztg. 1913, **37**, 1422. Spornitz: Ber. 1914, **47**, 2478. Chiris: Parf. France 1924, **2**, 234. Glichitch: Ibid. 1926, **4**, 253.

³ J. Chem. Soc. Japan 1932, **53**, 650.

RHIZOMES OF THE ARUM FAMILY

(*Araceæ*)

ONE aromatic rhizome, calamus, is described below. It consists largely of a spongy tissue of *starch cells* and *oleoresin cells* with fiber bundles and fibro-vascular bundles of several types.

Araceous corms, used as vegetables, are described in Volume II.

CALAMUS

Acorus Calamus L.

Fr. Acore vrai. Sp. Calamo. It. Calamo. Ger. Kalmuswurzel.

The dried rhizome of sweet flag, or calamus, a plant with rushlike leaves growing wild in swamps of both Europe and the eastern United States, is the *rhizoma calami* of pharmacy. Japanese calamus, although regarded by some as a distinct species (*A. gramineus* Ait.), is stated by Russell¹ to be identical with European calamus, the slightly different values of the oil being due to other causes. After removal of a part of the volatile oil, the rhizomes are made into a confection. The volatile oil is used as a flavor for cordials and in perfumes.

MACROSCOPIC STRUCTURE.—Pieces of the fresh *rhizome* the size of a finger, because of the leaf-scar rings and the bases of the roots or the root scars, have a grublike appearance. Cut transversely, the white flesh is separated by a yellow endoderm, from one-half to one-third the distance to the center, into cortex and central cylinder.

MICROSCOPIC STRUCTURE (Fig. 31). **Epiderm** (*ep*).—On the internodes the cells are colorless, small, elongated, end to end in rows; on the leaf scars they are brown, isodiametric, polygonal.

Cortex (*C*).—For several rows the rounded polygonal cells of the starchy *ground tissue* form a close tissue, but further inward intercellular spaces appear, at first at the angles, and increase in size until the tissue consists of chains of cells about large spaces (*i*). Sometimes the cells show distinct pores. Most of the cells contain oval,

¹ J. Am. Chem. Soc. 1915, 37, 2387.

kidney-shaped, triangular, or irregular *starch grains* (*am*) up to 10μ , sometimes in aggregates, showing a very indistinct hilum. Polarization crosses are also indistinct.

Oleoresin cells (*ol*), recognized by the refraction of the contents and the crimson color taken on from safranin solution, occur in the chains of cells, sometimes at the angles, sometimes elsewhere. They may be either larger or smaller than the starch cells.

Bast fiber bundles (*f*) occur in the outer cortex, replaced further inward by *fibro-vascular bundles* of the collateral type with bast fiber sheaths. *Crystal fibers* are sometimes present.

An *endoderm* (*en*) with typical thickened radial walls, staining red with safranin, completes the cortex. The cells contain starch.

Central Cylinder (S).—A more or less distinct *pericycle* (*pc*) of thin-walled cells is also evident in cross section.

A *bundle zone* adjoins the pericycle, concentric, compound, and collateral fibro-vascular bundles being represented, the concentric predominating. The compound bundles are formed by the union of two concentric bundles, the vessels at the junction being lacking. Further inward all the bundles are concentric.

The *vessels* are spiral-reticulated, reticulated, and scalariform, up to about 30μ wide. Instead of bast fibers, groups of elongated, pitted, short pointed, or blunt cells adjoin the

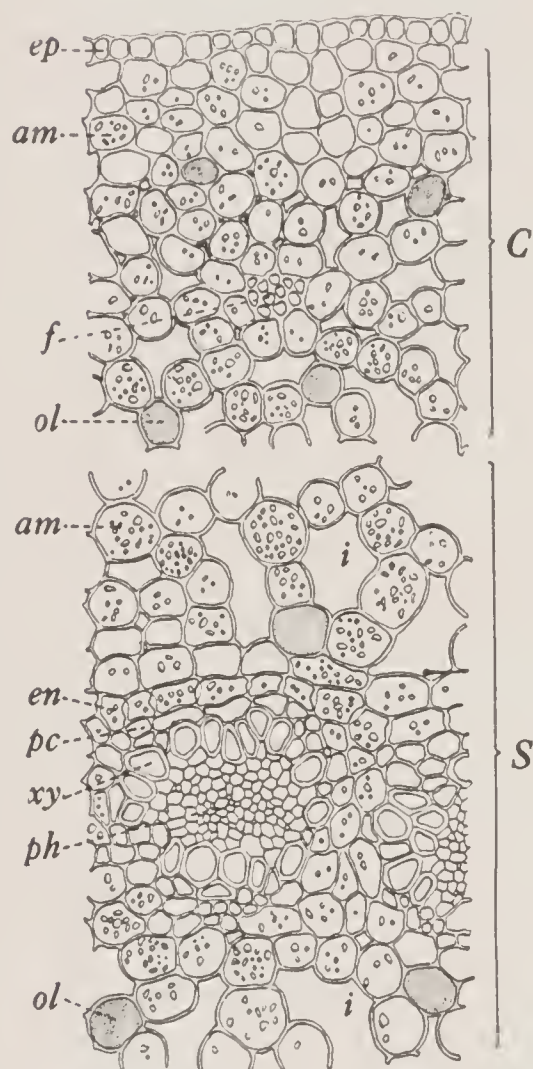


FIG. 31.—Calamus. Rhizome in cross section. *ep* epiderm. *C* outer cortex: *am* starch cells; *ol* oleoresin cells; *f* bast fiber bundle. *S* inner cortex and central cylinder: *en* endoderm; *pc* pericycle; concentric vascular bundle with *ph* phloem, *xy* xylem, and sclerenchyma cells; *i* intercellular spaces; *ol* oleoresin cells. $\times 160$. (A.L.W.)

more or less sclerenchymatized, short pointed, or blunt cells adjoin the vessels on the inside.

Chains of *starch cells* (*am*) and *oleoresin cells* (*ol*) form the ground tissue.

Root.—Radial bundles characterize the root. In mature roots the inner vessels of the xylem rays of the heptarch central cylinder touch one another, phloem alternating only between the angles on the outer side; in less mature roots they are separated to the pith by phloem rays.

CHIEF STRUCTURAL CHARACTERS.—Rhizome jointed, with endoderm showing in white flesh.

Epidermal cells elongated or isodiametric. Cortex and central cylinder with starch cells of ground tissue, mostly in chains, interspersed with oleoresin cells. Cortex with bast fiber bundles and collateral vascular bundles. Central cylinder with ring of concentric, compound, and collateral bundles and further inward concentric bundles, sclerenchyma cells replacing bast fibers. Root with radial bundles. All the fundamental types of bundles are represented in this plant.

CHEMICAL COMPOSITION.—No proximate analysis is available.

Volatile Oil. *Physical and Chemical Values.*—The limits for European and Japanese oils, compiled chiefly from Schimmel & Co. Reports,¹ follow:

VALUES OF EUROPEAN AND JAPANESE CALAMUS OIL

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Ester No.	Acetyl No.*	Acid No.
European:			°			
Min.	0.956	1.5028	+ 9	5	30	0
Max.	0.972	1.5098	+31	20	55	25
Japanese:						
Min.	0.973	1.511	+ 7	..†	..†	..
Max.	1.023	1.528	+27	..†	..†	..

* Ester number after acetylation. † Less than European.

The values, obtained by Russell² on oil from different parts of plants grown in the United States, appear in the table on the next page.

Russian oil, examined by Chernukhin,³ conforms to the above limits for European oil.

¹ Rep. Oct. 1894, table p. 8; Apr. 1895, 18; Apr. 1897, 9; Apr. 1915, 9.

² J. Am. Chem. Soc. 1915, **37**, 2387.

³ Trans. Sci. Chem. Pharm. Inst. (Moskow) 1928, **19**, 196 (in English 201).

VALUES OF AMERICAN CALAMUS OIL

Part of plant and yield	Sp. gr. 23° C.	Ref. ind. 23° C.	Opt. rot. 23° C.	Sapon. No.	Ester No.	Acetyl No.*	Acid No.
Madison, Wis.:			°				
Tops, fresh (0.123%).....	0.9509	1.5035	+12.2	12.6	53.05	0
Rhizomes, dried (0.638%)....	0.9547	1.4990	+21.7	15.5	38.40	0
Roots, dried (2.50%).....	0.9491	1.5065	+18.7	23.7	42.10	0
Bell, Md.:							
Rhizomes, air-dry (0.95%)....	0.9938	1.5140	63.45	55.3	8.15
Market:							
Rhizomes, dry (1.493%).....	0.9945	1.5080	48.25	42.5	8.75

* Ester number after acetylation.

Indian oil, prepared by Rao, Sudborough, and Watson,¹ showed specific gravity at 15° C. 1.069; refractive index at 20° C. 1.5048; optical rotation at 25° C. +6.2°; saponification number, direct 5.1, after acetylation 16.6; and soluble in 1.5 volumes of 70 per cent alcohol.

Constituents.—Thoms and Beckstroem² found, in high-boiling-point fractions of Japanese oil, *calameone* (C₁₅H₂₆O₂) and *asarone* (C₁₂H₁₆O₃), also small amounts of *n-heptylic acid* (C₇H₁₄O₂), *palmitic acid* (C₁₆H₃₂O₂), an *unsaturated acid* (C₁₆H₂₈O₂), and *eugenol*. *Calameone*, previously described by Schimmel & Co.³ and Von Soden and Rojahn⁴ as calamus camphor, forms glistening rhombic crystals melting at 128° C.; asarone, or propenyl-trimethoxybenzol, forms monoclinic crystals melting at 61° C.

In Japanese oil, Asahina⁵ identified *methyl eugenol*, present in the high-boiling-point fraction, and Asahina and Imai⁶ a *tricyclic sesquiterpene* (C₁₅H₂₅).

Semmler and Spornitz,⁷ in Russian calamus oil, isolated *d-α-pinene*, the presence of which was suggested by Kurbatow,⁸ *camphene*, *camphor*, a sesquiterpene *calamene* (C₁₅H₂₄), and a sesquiterpene alcohol *calamenenol* (C₁₅H₂₄O), but questioned the presence, as a natural constituent, of the hydrocarbon calamenene (C₁₅H₂₂) described by Thoms and Beckstroem.

¹ J. Indian Inst. Sci. 1925, 8A, 143.

² Ber. 1901, 34, 1021; 1902, 35, 3187.

³ Rep. Oct. 1899, 8.

⁴ Pharm. Ztg. 1901, 46, 243.

⁵ Apoth. Ztg. 1906, 21, 987.

⁶ J. Pharm. Soc. Japan 1914, 393, 1257.

⁷ Ber. 1913, 46, 3700.

⁸ Ibid. 1873, 6, 1210.

In the Indian oil noted above, pinene, camphene, and camphor appear to have been absent.

Acorin, $C_{36}H_{60}O_6$, a bitter principle, was separated from the rhizome by Thoms.¹ He disagrees with Genther,² who found it to contain nitrogen, and with Faust,³ who believed it to be a glucoside. On boiling with acid it splits up into a volatile oil and a resinous substance, acoretin.

Pentosans.—In dry matter 8.86 per cent. See Introduction.

¹ Arch. Pharm. 1886, **24**, 465.

² Ann. 1887, **240**, 92.

³ Arch. Pharm. 1867, **132**, 214.

RHIZOMES OF THE IRIS FAMILY

(*Iridaceæ*)

THIS family is represented by orris root, characterized by its violet odor, prismatic oxalate crystals, and truncated starch grains.

ORRIS

Iris florentina L.

Fr. Rhizome d'iris. Sp. Raiz de iris florentina. It. Radice di iris.
Ger. Veilchenwurzel.

The rhizome of the white flower-de-luce, well known in pharmacy and the perfumery industry, deserves a word of mention among foods since the powdered rhizome and the volatile oil, like the violet and its volatile oil which they resemble in odor, serve in the manufacture of confectionery and cordials.

MACROSCOPIC STRUCTURE.—The jointed, knotty appearance of the *rhizome* is well known to all familiar with an old flower garden, as it grows normally half out of the ground.

MICROSCOPIC STRUCTURE.—The striking features are (1) the long (up to 0.5 mm.) prismatic *crystals* of calcium oxalate, often with a fishtail or blunt pointed end, and (2) numerous elongated (up to 50 μ) *starch grains* with a hilum at one end and a truncation at the other where the leucoplast was attached; also small *starch grains*, often in rod-shaped aggregates.

CHEMICAL COMPOSITION.—In addition to an abundant store of starch (15 to 20 per cent), the air-dry rhizome contains volatile oil (up to 0.2 per cent), resin, fatty oil, wax, tannin, fibrous and nitrogenous matter, the glucoside *iridin* ($C_{24}H_{26}O_{13}$), and ash (about 2 per cent). The total ether extract is about 2 per cent.

Volatile Oil. *Physical and Chemical Values.*—The distilled oil is semisolid, of a yellowish color. Schimmel & Co.¹ and Guenther² give its melting point as about 50° and 41.5 to 45° C. respectively. According to Guenther it has the following values: saponification number 205.3 to 209.3, acid number 198.8 to 205.8, and irone 13.4 to 15.4

¹ Rep. Apr. 1901, 44.

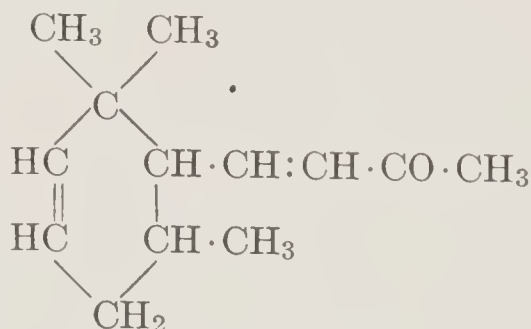
² Am. Perfumer 1935, 30, 17, 56.

per cent. The high saponification and acid numbers are due chiefly to myristic acid and in some degree to lower carbon acids which are removed by a subsequent process, yielding the "absolute essence" or "oil of orris tenfold." The figures given by Schimmel & Co. for what appears to be this product and by Guenther for one so designated are respectively as follows: specific gravity at 15° C. 0.93 to 0.94, 0.938 to 0.941; refractive index at 20° C. 1.492 to 1.500, 1.4950 to 1.4975; optical rotation +14 to +30°, +34 to +38°; saponification number —, 18.7 to 29.9; ester number 20 to 40, —; acid number 1 to 8, 1.4 to 8.4; irone —, 72.0 to 79.7 per cent; soluble in 80 per cent alcohol 1 to 1.5, 1 to 1+ volumes.

Constituents.—The odorous constituent is a ketone, *irone* ($C_{13}H_{20}O$), first isolated by Tiemann and Krüger;¹ the most abundant constituent is *myristic acid*, which, together with its methyl ester, makes up 80 to 90 per cent of the oil. Small amounts of *oleic acid* and its ester and aldehyde were obtained by Tiemann and Krüger.¹ Schimmel & Co.² report *n-decylic aldehyde*, *nonylic aldehyde*, *furfural*, *benzaldehyde*, *naphthalene*, a ketone with the formula $C_{10}H_{18}O$, and traces of other constituents.

More recently Langlais and Goby³ have announced the presence of *octylic* (caprylic), *nonylic* (pelargonic), *decylic* (capric), *undecylic*, *duodecylic* (lauric), *tridecylic*, and *benzoic acids*. The acids with nine, eleven, and thirteen carbon atoms in the molecule had not previously been found in natural substances.

Of importance as a perfume and flavor is synthetic *ionone*, consisting of α - and β -forms in different proportions, both being isomers of irone, but according to Tiemann and Krüger,⁴ with the double bond of the ring between carbon atoms 3 and 4 and 2 and 3 respectively, the hydrogen atoms being arranged accordingly. The structural formula of irone follows:



Irone

¹ Ber. 1893, 26, 2675.

² Rep. Apr. 1907, 76.

³ Parf. France 1924, 19, 256.

⁴ Ber. 1893, 26, 2675.

RHIZOMES OF THE GINGER FAMILY

(*Zingiberaceæ*)

COMMON ginger is the only species of considerable importance of the genus *Zingiber*. The genus *Curcuma* is represented by turmeric (*C. longa* L.) and several lesser-known species such as zedoary (*C. Zedoaria* Rose.) and round zedoary (*C. aromatica* Salisb.), and the genus *Alpinia* by the species galangal (*A. officinarum* Hance) and others.

Only ginger and turmeric are described below.

COMPARATIVE MACROSCOPIC STRUCTURE.—The *rhizomes* of ginger are flattened, branching, with indistinct rings and light buff flesh; those of turmeric are round or elongated with deep orange flesh. Both show in cross section an endoderm and numerous vascular bundles in both cortex and central cylinder.

COMPARATIVE MICROSCOPIC STRUCTURE.—The elements common to both rhizomes are *cork cells*, polygonal in surface view, *starch* of the ground tissue, *oleoresin cells* of the cortex and central cylinder, *endoderm*, and *scalariform* and *spiral-reticulated vessels* of the fibro-vascular bundles. Perfect *starch grains* occur only in ginger, those of turmeric being gelatinized. *Bast fibers* occur only in ginger, and there only in the central part of the central cylinder.

Curcumin, present in the oleoresin cells of turmeric, gives characteristic reactions.

GINGER

Zingiber officinale Rose.

Fr. Gingembre. Sp. Gengibre. It. Zenzero. Ger. Ingwer.

True ginger (*Z. officinale*) has been so long in cultivation that its original habitat is obscure; most authors, however, state it to be tropical Asia. Hartwich and Swanlund¹ refer to three other species: (1) *Z. Zerumbet* Rose. with thicker but less pungent rhizomes, grown in southeastern Asia, (2) *Z. Mioga* Rose. with much thicker rhizomes having a bergamotlike flavor, grown in Japan and China, and (3)

¹ B. deut. pharm. Ges. 1903, 142.

Z. Cassumunar Roxb. with yellow rhizomes with a camphorlike flavor, grown in India.

Watson¹ states that the ginger of Siam, with a very thick, little-flattened, sparingly branched rhizome, is from *Alpinia Allughas*.

The spice comes into the market in three forms: (1) undecorticated or black ginger, (2) scraped, and (3) bleached or coated. African or Sierra Leone and Calcutta or East Indian belong to the first class, the rhizomes being of an unattractive brown color. Jamaica, Cochin, and Japan ginger are commonly scraped and often bleached or coated in addition.

Chloride of lime, sulphurous acid, and alkali sulphites are used for bleaching. Coating with chalk or plaster or dipping in lime water is practiced not merely to improve the appearance but also to ward off attacks of insects such as the drugstore beetle which, unchecked, soon reduce the rhizome to an unsightly powder.

Ginger is used in a greater variety of ways than most spices. Dry ginger is used whole in pickles and ground in cakes, pies, and various sweetmeats. From the dry ginger is prepared ginger extract, and from this in turn ginger cordial. Ginger ale is the most widely used bottled, carbonated non-alcoholic beverage. In China, ginger root is candied or preserved while fresh ("green") in honey or sugar sirup and exported to all parts of the world. Whole undried ginger is also one of the chief constituents of canned mixed pickles put up in Canton and sold extensively in the Chinese quarters of American cities. It may accordingly be stated that, unlike other spices, ginger is consumed as a spice, as a beverage, and as a food proper.

MACROSCOPIC STRUCTURE.—Arthur Meyer² was the first to study carefully the system of branching of the *rhizome*, known commercially as ginger root, which is technically a sympodium. The branches are formed only on the narrow sides of the somewhat flattened organ, and only those on the under side reach any considerable size. Several branches form on the under side of the first joint, further elongation being carried on by the end branch, which in turn branches like the first, and so on. The lower branches of each joint form secondary and even tertiary branches in like manner.

Leaf scars form delicate rings about the rhizome; scars of the stems occur as rather large depressions at the end of some of the branches, while small scars mark the position of the roots which are detached in trimming for the market.

¹ Pharm. J. 1886, 17, 127.

² Arch. Pharm. 1888, 218, 419.

Uncorticated ginger (Fig. 32, left) is characterized by the loose cork, especially on the narrow sides; scraped ginger (Fig. 32, right), by the bundles exposed by removal of the cortex. Cochin and Japan ginger have rather thick joints; Jamaica, comparatively slender.

On breaking the rhizome, bundles are seen to protrude; on cutting crosswise, the oval surface (Fig. 33) shows the *cork* (*Su*) tissue beneath the *epiderm* (*Ep*) and *hypoderm* (*H*), the *cortex* (*C*) with the *endoderm* (*En*), and the *central cylinder* (*S*), both cortex and central cylinder being dotted with bundles.

MICROSCOPIC STRUCTURE.—Ginger is described more or less fully in all works on the microscopy of drugs and foods. Cross sec-

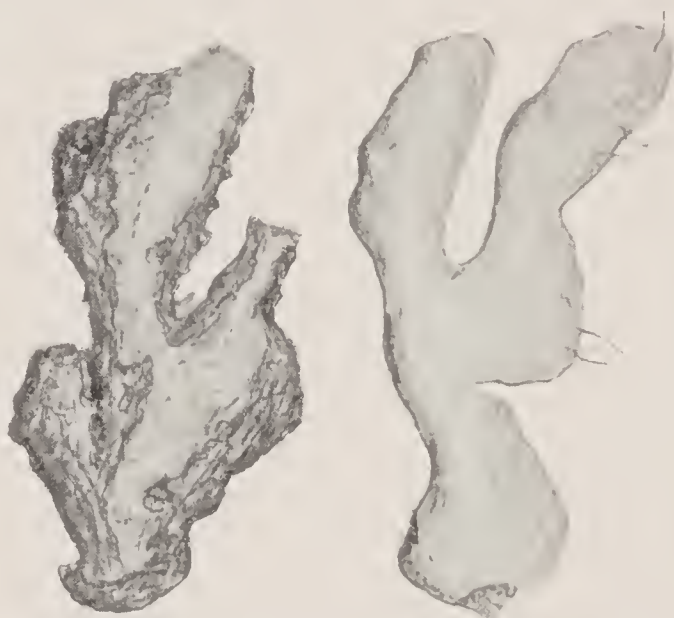


FIG. 32.—Ginger. Rhizomes. Left: African (untreated). Right: Jamaica (decorticated and limed). $\times 1$. (A.L.W.)

tions should be cut from an uncorticated rhizome and soaked for some hours in 1 per cent sodium hydroxide to expand the collapsed cells of the endoderm, pericycle, and phloem groups. Scraped ginger naturally lacks some of the outer tissues.

Epiderm (Fig. 34, *ep*).—The cells are polygonal in surface view, tabular in cross section.

Hypoderm (Fig. 34, *hy*).—Several rows of cells, in surface view polygonal and larger than those of the epiderm, form the hypoderm. In cross section they lack the regular form and arrangement of the cork cells beneath.

Cork (Figs. 34 and 35, *su*).—In surface view the cells are polygonal; in cross section they are arranged in typical radial rows.

Cortex.—*Compressed parenchyma* (Fig. 34, *c*) forms the outer layers, passing further inward into typical *starch cells* (*am*). The

starch grains of the outer cortex are smaller than those of the inner cortex and the central cylinder. Here and there occur *oleoresin cells* (*ol*¹), the contents of which are red or brown, liquid or forming a solid mass.

Numerous *fibro-vascular bundles* run longitudinally through the cortex. These, as is true of other members of the family, are largely independent of the bundles of the central cylinder and not, as is true of bundles occurring in the cortex of many roots, tubers, and rhizomes, merely connecting links between those of the central cylinder and of the leaves or roots.

The *endoderm* (*en*), or inner layer of the cortex, consists of yellow flattened cells readily distinguished from the colorless polygonal cells of the ground tissue of the cortex. The radial walls, being suberized, stain a bright red with safranin, and the yellow color is intensified by chlorzinc iodine.

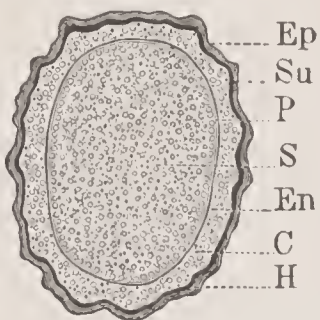


FIG. 33.

FIG. 33.—Ginger. Rhizome in cross section. *Ep* epidermis; *H* hypoderm; *Su* cork; *C* cortex with *En* endoderm; *P* pericycle; *S* central cylinder. Bundles shown as circles, oleoresin cells as black dots. $\times 2$. (A.L.W.)

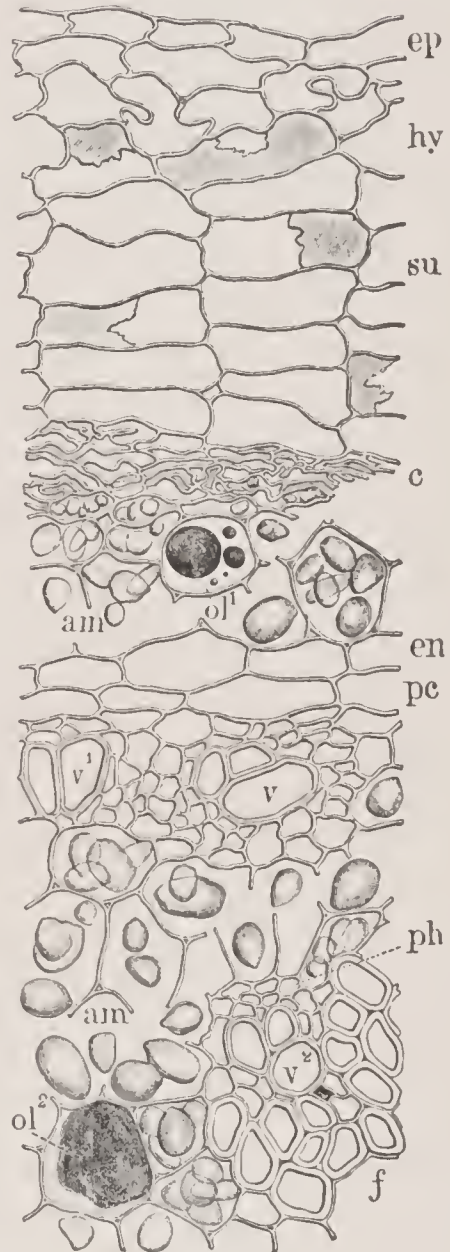


FIG. 34.

FIG. 34.—Ginger. Rhizome in cross section. *ep* epidermis; *hy* hypoderm; *su* cork cells; *c* outer cortex with compressed cells, *am* starch cells, and *ol*¹ oleoresin cells; *en* endoderm; *pc* pericycle; *v*, *v*¹ vessels of bundle ring; *v*² vessel, *ph* phloem, and *f* bast fibers of inner bundle; *ol*² oleoresin cell; *am* starch cells. $\times 160$. (A.L.W.)

Central Cylinder.—A single layer of cells, similar to those of the endoderm, forms the *pericycle* (Fig. 34, *pc*).

Immediately beneath the pericycle is an almost unbroken ring or zone of *fibro-vascular bundles* in which scalariform, spiral-reticulated, and less often spiral vessels (Fig. 34, *v*, *v*¹; Fig. 35, *sca*), although not numerous, are conspicuous; bast fibers, however, are lacking. The bundles further inward are separated by ground parenchyma, those in the central portion having groups of typical *bast fibers* (*f*) partly surrounding the vessels. The bast fibers have walls much narrower than the lumen, with diagonal pores. Many of the vessels and bast fibers are not strongly lignified, staining blue with chlorzine iodine.

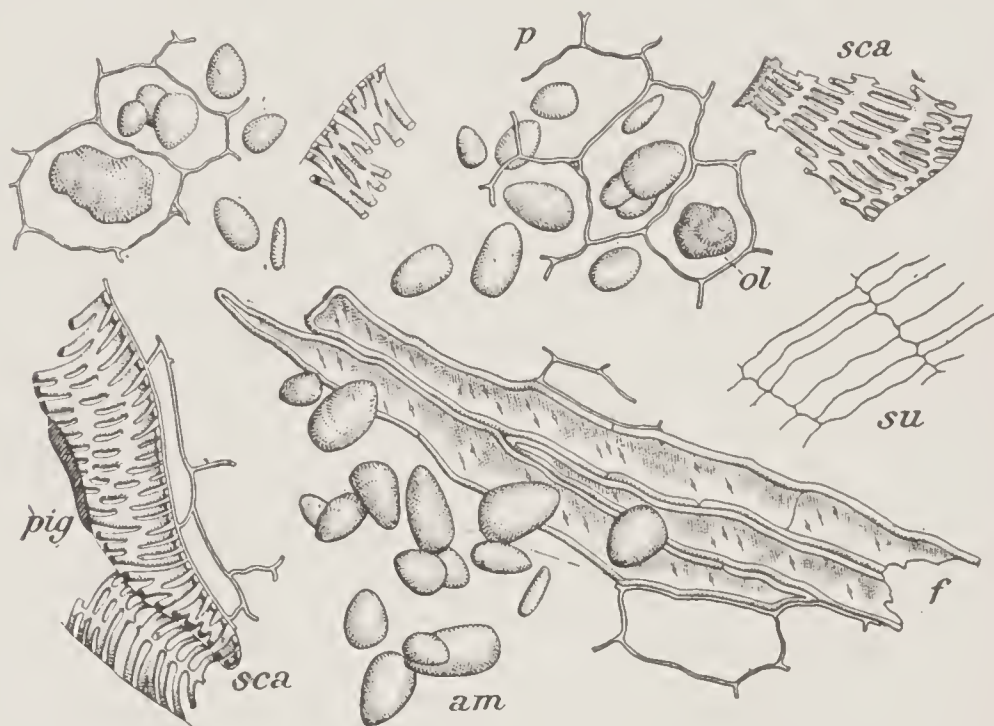


FIG. 35.—Ginger. Elements of powder. *su* cork; *p* parenchyma with starch grains and *ol* oleoresin; *sca* vessels; *pig* pigment cell; *f* bast fibers; *am* starch grains. $\times 160$. (K.B.W.)

Accompanying the vessels are often narrow elongated *pigment cells* filled with a dark substance. One of these is shown in Fig. 34 at the right of *v*² and another in Fig. 35, *pig*.

The *starch grains* (*am*) occurring in the ground parenchyma are like those of the inner cortex. The typical form is flattened, oval or ovate, more or less elongated (maximum length $45\ \mu$) but almost always with a distinct rounded angle at the narrower end. Neither rings nor hilum is usually evident.

Hanausek described in 1883 a variety of Japan ginger, the starch of which differed from the type in that (1) the large grains had very distinct rings and (2) the small grains were in aggregates. The writers

have observed that some lots of Japan ginger have aggregates but have been unable to decide definitely whether this is due to botanical variety or species or to conditions of growth. Rhizomes, like roots but unlike fruits and seeds, are gathered at different stages of development, hence the difficulty of making statements as to size and other characters of the starch grains which are applicable in all cases. Examination of authentic rhizomes of the different species furnishing commercial ginger, grown under observation, can alone determine the reason for characters such as Hanausek observed.

Oleoresin cells (*ol*²) occur here and there.

CHIEF STRUCTURAL CHARACTERS.—Rhizome branching, forming sympodium, often scraped, bleached, or coated. Bundles in cortex and central cylinder, also endoderm, evident in cross section.

Epiderm, hypoderm, and cork with polygonal cells. Cortex and central cylinder with ground tissue of starch parenchyma and oleoresin cells. Starch grains flattened, oval or ovate, up to 45 μ , with hilum (located by polarization) in small, rounded-angular end. Endoderm and pericycle evident in cross section. Bundles partly in ring immediately within pericycle and partly distributed through ground parenchyma of cortex and central cylinder. Vessels scalariform or spiral-reticulated; bast fibers only in central bundles.

MICROSCOPY OF GROUND GINGER.—The addition of cereal biscuit colored with iron oxide may be detected by the distorted starch grains and the bran tissues.

CHEMICAL COMPOSITION.—The general proximate composition of ginger of different commercial varieties is brought out by analyses, tabulated herewith, made by Winton, Ogden, and Mitchell,¹ Reich,² and Kraemer and Sindall,³ all of whom worked on samples ground in the laboratory and, so far as they determined the same constituents, used essentially the same methods.

Fixed and volatile oils were determined by continuous ether extraction, evaporation of the ether at room temperature, drying over sulphuric acid to secure the total extract, and at 100° and then at 110° C. to drive off the volatile oil, the method being that proposed by Richardson.⁴ Alcohol extraction was carried out by shaking 2 grams of the material with 100 cc. of 95 per cent alcohol at room temperature

¹ Connecticut Agr. Exp. Sta. Rep. 1898, p. 184.

² Z. Unters. Nahr.-Genusssm. 1907, **14**, 549.

³ Am. J. Pharm. 1908, **80**, 303.

⁴ U. S. Dept. Agr., Div. Chem. 1887, Bul. **13**, II, 165.

COMPOSITION OF GINGER AND BY-PRODUCTS (WINTON, OGDEN, AND MITCHELL)

	Water	Pro- tein (N× 6.25)	Oil, fixed*	Oil, vola- tile†	Starch, crude ‡	Starch, pure §	Fiber	Ash, total	Ash, sol- uble	Sand	Lime (CaO)
	%	%	%	%	%	%	%	%	%	%	%
Jamaica:											
Limed											
Min.	10.56	9.00	2.82	1.21	56.00	53.95	2.37	7.28	2.32	0.02	1.92
Max.	10.57	9.69	3.43	1.34	58.63	55.61	2.38	9.35	2.95	0.03	3.53
Aver. (2)	10.56	9.34	3.12	1.27	57.31	54.78	2.37	8.31	2.63	0.02	2.72
Natural											
Min.	10.27	6.25	3.82	1.61	56.31	55.05	3.17	3.61	2.64	0.05	0.20
Max. . .	11.72	9.75	3.97	2.01	58.41	57.10	4.28	4.72	3.40	0.51	0.30
Aver. (3)	11.22	7.85	3.91	1.79	57.59	56.09	3.72	4.17	2.96	0.22	0.26
Cochin:											
Limed	9.97	7.50	2.95	1.49	62.42	60.31	2.60	5.36	2.95	0.08	1.29
Rough	9.96	8.00	4.50	2.47	56.65	53.94	4.22	3.81	2.42	0.12	0.24
A, B, C											
Min.	10.33	8.06	3.64	1.86	58.43	56.62	3.57	3.66	2.18	0.06	0.25
Max.	10.54	8.25	3.75	2.32	59.73	58.05	3.68	4.06	2.62	0.15	0.71
Aver. (2)	10.43	8.15	3.70	2.09	59.08	57.33	3.62	3.86	2.40	0.10	0.48
D											
Min.	8.71	7.81	5.08	2.52	53.43	49.05	5.10	4.96	2.67	0.23	0.55
Max.	9.91	7.88	5.15	3.09	53.97	49.86	5.50	5.48	2.89	0.68	0.56
Aver. (2)	9.31	7.84	5.11	2.80	53.70	49.45	5.30	5.22	2.78	0.45	0.55
Japan:											
Limed											
Min.	11.13	4.81	3.86	0.96	60.08	55.40	2.62	4.34	1.73	0.15	1.07
Max.	11.65	6.00	4.02	0.96	61.02	58.70	2.84	8.04	1.89	1.28	2.26
Aver. (2)	10.39	5.40	3.94	0.96	60.55	57.05	2.73	6.19	1.81	0.71	1.66
African:											
Min.	9.89	7.88	5.28	2.60	55.65	51.60	4.31	3.61	2.17	0.08	0.21
Max. . .	10.03	7.94	5.42	2.94	57.42	53.36	4.93	4.24	2.73	0.14	0.28
Aver. (3)	9.97	7.92	5.35	2.73	56.74	52.68	4.66	4.00	2.52	0.11	0.25
Calcutta:											
Min.	10.19	7.25	3.37	1.73	55.39	51.24	5.08	6.47	3.60	1.74	0.26
Max.	10.86	7.69	3.52	1.84	55.62	52.48	5.37	7.55	4.09	2.29	0.27
Aver. (2)	10.52	7.47	3.44	1.78	55.50	51.85	5.22	7.01	3.84	2.01	0.26
All above											
Min.	8.71	4.81	2.82	0.96	53.43	49.05	2.37	3.61	1.73	0.02	0.20
Max.	11.72	9.75	5.42	3.09	62.42	60.31	5.50	9.35	4.09	2.29	3.53
Av. (18)	10.44	7.74	4.10	1.97	57.45	54.53	3.91	5.27	2.71	0.44	0.80
Waste:											
Scrappy	4.99	7.00	9.55	6.05	31.38	19.35	13.18	8.05	4.03	0.89	0.61
Cuttings	3.19	8.69	2.76	7.06	40.23	31.14	8.69	9.20	3.90	1.81	1.06
Spent I¶	10.61	6.94	3.86	1.61	59.86	54.57	5.17	2.12	0.59	0.18
Spent II**	8.02	0.54	0.13	5.05	3.55	1.50

* Non-volatile ether extract. † Volatile ether extract. ‡ Reducing matter, after washing with 10% alcohol and direct inversion of residue, calculated as starch. § Diastase method. || Also scraped. ¶ Residue from ginger alc manufacture. ** Residue from ginger extract manufacture.

during 8 hours, then allowing to stand 16 hours, and filtering as proposed by Winton. Reich followed the same manipulation in determining methyl alcohol and petroleum ether extract, and Winton, Og-

COMPOSITION OF GINGER AND SPENT GINGER (REICH)

	Water	Oil, fixed*	Oil, vola- tile†	Alcohol (after ether) extract	Alcohol extract	Methyl alcohol extract	Petro- leum ether extract	Ash, total	Ash, sol- uble	Sand
	%	%	%	%	%	%	%	%	%	%
Cochin:										
Min.	10.40	3.02	1.05	1.49	3.49	4.14	1.95	3.33	1.64	0.05
Max.	12.59	3.77	1.65	2.11	4.54	4.94	2.49	4.98	2.96	0.20
Aver. (13)	11.64	3.40	1.38	1.86	3.96	4.43	2.19	4.18	2.33	0.15
Japan:										
Min.	9.20	3.72	0.90	2.69	5.08	6.26	2.51	3.24	1.52	0.14
Max.	13.80	5.16	1.98	4.46	6.44	7.86	3.72	6.44	3.04	0.52
Aver. (10)	11.68	4.48	1.38	3.45	5.80	7.19	3.06	4.65	2.04	0.30
African:										
Min.	11.16	5.66	2.10	1.39	5.80	6.22	3.19	3.29	1.63	0.08
Max.	13.65	8.08	3.08	2.42	8.05	9.58	5.77	6.22	2.56	2.47
Aver. (9)	12.74	6.50	2.54	1.70	6.64	7.47	4.64	4.37	1.97	0.84
Bengal:										
Min.	11.69	2.84	1.17	1.21	3.24	3.82	1.96	5.48	2.56	1.21
Max.	13.85	4.94	2.15	2.98	5.35	6.46	3.09	9.33	4.51	3.79
Aver. (18)	12.51	3.97	1.60	1.88	4.36	5.43	2.46	7.06	3.45	2.05
Spent ginger:										
Extracted‡										
Min.	9.74	0.67	0.14	0.55	0.90	1.54	0.35	3.28	0.99	0.11
Max.	13.42	1.32	0.48	1.80	1.50	1.90	0.69	4.52	2.73	0.97
Aver. (3)	12.14	1.06	0.36	1.01	1.23	1.74	0.53	4.01	1.88	0.48
Slops§	12.33	5.05	0.52	1.76	4.97	4.90	2.19	5.26	2.02	0.74

* Non-volatile ether extract. † Volatile ether extract. ‡ Residue after alcohol extraction.
§ Factory residue after distilling off volatile oil.

den, and Mitchell in determining cold water extract. Soluble ash was determined as described under Pepper. The other methods need no explanation other than indicated by the headings and the footnotes to the tables.

The results on fiber, supplemented by those on ash and sand, are of value in determining whether or not the rhizomes had been scraped or peeled and to what extent. African and Calcutta ginger, characterized by their dark color, also most grades of the lighter-colored Cochin variety, are not scraped. Coating is indicated by an abnormal percentage of lime. Reich found that the coating of the Cochin ginger examined by him was calcium sulphate, while that of the Japan ginger was calcium carbonate. He did not examine Jamaica ginger, which is usually coated with the carbonate to an extent shown by the analyses of Winton, Ogden, and Mitchell. There appears to be no correlation between bleaching and composition as usually determined.

The results on alcohol extract bring out strikingly the difference between natural ginger and spent ginger from the manufacture of

ginger extract. For example, Winton, Ogden, and Mitchell found 3.63 to 6.58, aver. **5.18**, per cent of alcohol extract in natural ginger but only 1.52 per cent in spent ginger from an extract works, and Reich records similar results. Cold water extract, employed by English analysts in differentiating natural ginger and the residue from the manufacture of ginger ale, amounted in analyses by Winton et al. to 10.92 to 17.55, aver. **13.42**, per cent in natural ginger but only to 6.15 per cent in the residue from a ginger ale works.

COMPOSITION OF GINGER (KRAEMER AND SINDALL)

	Oil, fixed*	Oil, vola- tile†	Starch, erude	Fiber	Alcohol extract	Cold water extract	Ash, total	Sand	Lime (CaO)
	%	%	%	%	%	%	%	%	%
Jamaica:									
Min.	43.64	4.32	3.72	0.16
Max.	62.97	5.80	4.15	0.45
Aver.	7.30‡	3.23‡	56.42	1.44‡	4.95	15.54‡	3.90	0.24	0.17‡
Calicut:									
Min.	48.33	7.00	5.51	0.55
Max.	48.77	8.16	5.64	0.69
Aver.	6.42‡	4.62‡	48.55	1.64‡	7.64	13.08‡	5.56	0.61	0.33‡
Cochin:									
Min.	40.39	5.40	6.31	0.79
Max.	52.00	8.04	6.43	0.92
Aver.	6.68‡	7.03‡	44.40	3.06‡	6.32	14.30‡	6.36	0.86	0.58‡
Japan:									
Min.	39.99	6.96	6.02	0.61
Max.	55.97	10.48	6.40	0.72
Aver.	7.01‡	7.39‡	50.60	1.60‡	8.37	14.40‡	6.14	0.66	1.68‡
African:									
Min.	48.99	5.68	5.60	1.06
Max.	57.09	7.20	5.74	1.29
Aver.	8.49‡	7.17‡	53.71	2.62‡	6.36	12.62‡	5.64	1.16	0.12‡
Caleutta:									
Min.	47.89	5.28	7.14	2.02
Max.	60.75	6.40	7.75	2.31
Aver.	6.50‡	3.06‡	52.60	5.46‡	5.69	14.20‡	7.45	2.15	0.13‡

* Non-volatile ether extract. † Volatile ether extract. ‡ 1 sample.

U. S. Standards.—Ginger, washed and dried, or decorticated and dried: not less than 42 per cent of starch, 12 per cent of cold water extract, nor 2 per cent of cold-water-soluble ash; not more than 8 per cent of fiber, 1 per cent of lime (CaO), 7 per cent of total ash, nor 2 per cent of sand. Jamaica ginger: not less than 15 per cent of cold water extract; otherwise as for ginger. Limed ginger, bleached ginger: not more than 4 per cent of carbonate of calcium nor 10 per cent of

total ash; otherwise as for ginger. Ginger extract contains in each 100 cc. of the alcohol-soluble matters not less than 20 grams of ginger.

Proteins.—So far as the writers are aware, no studies of the individual proteins of ginger have been undertaken.

Fixed Oil.—About two-thirds of the ether extract is not driven off on heating at 100° and then at 110° C. In addition to fatty oil and resins this non-volatile or fixed oil contains pungent principles to which ginger owes its sharp taste but not its fragrance.

Zingerone or *3-methoxy-4-hydroxy phenyl ethyl methyl ketone*, $C_{11}H_{14}O_3$ or $3,4-CH_3O(HO)C_6H_3CH_2CH_2COCH_3$. Thresh,¹ in a series of papers published from 1879 to 1884, describes a non-volatile pungent extract, *gingerol*, which he obtained in the form of a thick, light yellow oil from a 95 per cent alcohol percolate. This oil is soluble in ether and other fat solvents as well as in alcohol, even as dilute as 50 per cent, as is also paradol, the corresponding pungent extractive of grains of paradise. The gingerol content of ginger is given as 0.50 to 1.50 per cent.

Garnett and Grier² distilled gingerol (which they did not regard as a simple compound) under diminished pressure, but the distillate appeared to contain decomposition products.

Nelson,³ following the method developed by earlier workers, prepared gingerol and paradol with the following values respectively: specific gravity 20°/20° 1.0713, 1.0690; optical rotation +12.9°, +9.2°; and refractive index at 20° 1.5212, 1.5232. By methylation of gingerol he secured a crystalline derivative having essentially the same composition and properties as the methyl-gingerol of Lapworth and co-workers. Having learned that these workers had synthesized and established the constitution of the pungent principle, Nelson discontinued his work.

H. Nomura⁴ and Lapworth and co-workers,⁵ working independently and during the same year, discovered *zingerone*, the chief pungent principle in gingerol. Although Nomura, who separated zingerone from a cold ether extract, appears to have been the first to publish, he abandoned his early name, zingiberone, in favor of Lapworth's name zingerone, thus avoiding confusion with Brooks's zingiberol. As Nelson resigned the field to Lapworth, so also in turn did

¹ Pharm. J. [3] 10 to 15.

² Ibid. 1907, 79, 118.

³ J. Am. Chem. Soc. 1917, 39, 1466.

⁴ Sci. Rep. Tohoku Imp. Univ. 1917, 6, 41, 375.

⁵ J. Chem. Soc. 1917, 111, 777.

Lapworth yield to Nomura, who published several articles on the pungent principles of ginger, as well as on zingerone and its homologs, and also patented his method of synthesis of zingerone.

Zingerone is a ketone. The needle-shaped crystals melt at 40 to 41° C. It forms a red coloration with Millon's reagent, a green coloration with alcoholic ferric chloride, and reduces ammoniacal silver nitrate solution, but is not perceptibly altered by shaking for some hours with 2 per cent sodium hydroxide solution. The yield obtained by Nomura from ginger was 0.04 per cent, but the actual content was doubtless greater.

Lapworth, Pearson, and Royle,¹ by extracting ginger with 35 per cent alcohol, obtained an extract which on purification yielded gingerol, boiling at 135 to 140° C. with slight decomposition. From gingerol they prepared methyl gingerol ($C_{18}H_{28}O_4$ or $C_{19}H_{30}O_4$) in the form of needles melting at 64° C. and decomposing somewhat below its boiling point. On distilling gingerol first *in vacuo* and then in steam, thus removing *heptylaldehyde*, a volatile oil, a residue was obtained from which zingerone was crystallized on seeding with crystals obtained synthetically as described by Lapworth and Wykes.² Methyl gingerol, although not shown to occur as such in ginger, is of interest because of its relation to actual constituents. According to Nomura and Iwamoto³ and Nomura, Iwamoto, and Muraami⁴ it probably has the structural formula $(CH_3O)_2C_6H_3CH_2CH_2COCH_2CH(OH)(CH_2)_4CH_3$.

Shogaol, $C_{17}H_{24}O_3$, a name derived from the Japanese word for ginger, is believed to be 3-methoxy-4-hydroxy-phenyl-ethyl-heptenyl ketone, an unsaturated ketone. It was first obtained by Nomura⁵ in a 175 to 185° fraction from a cold ether extract of ginger after separation of zingerone and was afterwards synthesized from zingerone by Nomura and Tsurumi.⁶ The substance is a light yellow liquid having a specific gravity at 25° C. of 1.0448 and a refractive index at 25° C. of 1.5241. Like zingerone it gives a green color with ferric chloride and reduces ammoniacal silver nitrate. No crystalline derivative has been reported.

Volatile Oil.—The aroma of ginger is due to one or more constituents of the volatile oil as distinguished from the pungent principles

¹ J. Chem. Soc. 1917, 111, 777.

² Ibid. 790.

³ Sci. Rep. Tohoku Imp. Univ. 1928, 17, 973.

⁴ Ibid. 1929, 18, 661.

⁵ Sci. Rep. Tohoku Imp. Univ. 1918, 7, 67.

⁶ Ibid. 1927, 16, 581.

which are non-volatile. According to Schimmel & Co. the volatile oil varies from 2.6 per cent in African to 1.8 per cent in Japan ginger. Zäch,¹ by the Von Fellenberg chromic acid oxidation method, obtained 0.8 to 3.0 per cent.

Physical and Chemical Values.—The usual values given in standard works are: specific gravity at 15° C. 0.875 to 0.900, optical rotation -45 to -25° , but these limits are sometimes exceeded. Gilde-meister and Hoffmann² give refractive index at 20° C. 1.489 to 1.494, acid number up to 2, ester number 0 to 15, ester number after acetylation 24 to 50, and soluble in 7 volumes or more of 95 per cent alcohol.

Moudgill³ found that the volatile oil from ginger scrapings, although about normal in specific gravity, showed an optical rotation at 30° of -9.85° , while that from a sample of Seychelles ginger,⁴ although otherwise normal, had a specific gravity at 15°/15° of 0.905. Moudgill found the refractive index of the volatile oil from green ginger and ginger scrapings at 28° to be 1.4878 and 1.4862 respectively. Volatile oil from Philippine ginger, examined by Valenzuela,⁵ showed acid number 2.22, ester number 32.8, and ester number after acetylation 88.3, while that from Seychelles ginger noted above showed ester number 22.5.

Constituents.—The chief constituents of volatile ginger oil are the sesquiterpene *zingiberene*, discovered by Von Soden and Rojahn,⁶ the terpenes *d-camphene* and β -*phellandrene*, also small amounts of *decylic aldehyde*, and the sesquiterpene alcohol *zingiberol*. All these are described below. Thresh⁷ found *cymene* and traces of other substances. Schimmel & Co.⁸ and Brooks⁹ report *cineol*, *citral*, and *borneol*, and Brooks also *methyl heptenone*, *nonylaldehyde*, *linaloöl*, *acetic* and *caprylic esters*, and a trace of a phenol, probably *chavicol*. Lapworth, Pearson, and Royle¹⁰ separated a small quantity of *heptyl-aldehyde* ($C_6H_{13}CHO$).

Zingiberene, $C_{15}H_{24}$, is a sesquiterpene allied to the caryophyllene

¹ Mitt. Lebensm. Hyg. 1932, **23**, 156.

² Ätherischen Öle, Leipzig, 3 Aufl. 1929, **2**, 438.

³ J. Indian Chem. Soc. 1928, **5**, 251.

⁴ Bul. Imp. Inst. 1926, **24**, 649.

⁵ J. Am. Pharm. Ass. 1926, **15**, 652, 734.

⁶ Pharm. Ztg. 1900, **45**, 414.

⁷ Pharm. J. 1881, [3], **12**, 243.

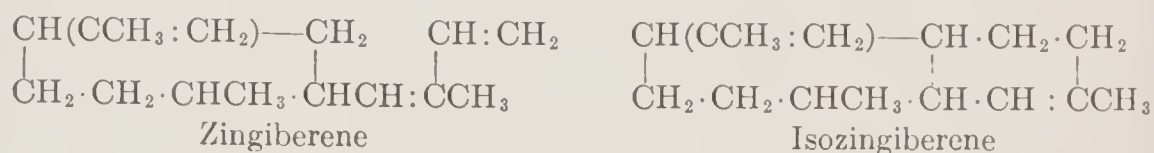
⁸ Rep. Oct. 1905, 38.

⁹ J. Am. Chem. Soc. 1916, **38**, 430.

¹⁰ Loc. cit.

of oil of cloves and its isomer clovene. Thresh¹ showed that the bulk of the volatile oil is a sesquiterpene boiling at 256 to 266° C. Von Soden and Rojahn¹ separated it in a purer form with a boiling point of 269 to 270° C. and gave it the name zingiberene. Its specific gravity is given as 0.872 to 0.873 at 15° C.; its optical rotation as -73.4°. Schreiner and Kremers² found the boiling point at 32 mm. to be 160 to 161° C. It has little or no odor.

Semmler and Becker³ showed that zingiberene on inversion with 50 per cent sulphuric acid in glacial acetic acid yields isozingiberene. They give the following as the probable structural formulas:



d-Camphene, C₁₀H₁₆, a solid melting at 48 to 50° C., was separated from the 155 to 165° fraction by Bertram and Walbaum.⁴ Its specific gravity at 20° C. is about 0.870. The source or method of synthesis of camphene determines whether it is dextrorotatory or levorotatory or inactive, but all three forms have the same chemical properties.

α -Phellandrene, C₁₀H₁₆, was separated by Bertram and Walbaum from the 170° fraction. Its specific gravity at 20° C. is 0.842. The terpene exists as α - and β -modifications, and each may be dextro- or levorotatory according to the source or method of synthesis.

Decylic Aldehyde, C₁₀H₂₀O₂.—Dodge,⁵ on fractioning the volatile oil of Jamaica ginger by steam or *in vacuo*, found that the first portion contained an aldehyde amounting to 2 to 5 per cent which corresponds in its composition and properties to decylic aldehyde.

Zingiberol, C₁₅H₂₆O, isolated by Brooks,⁶ is a sesquiterpene alcohol which he states is the only constituent of the oil that has the peculiarly characteristic fragrance of ginger, although other constituents may contribute to the composite odor. The substance boils at 154 to 157° at 14.5 mm., and the yield was 16 per cent of the volatile oil. Sodium in dry ether combines with the substance, and potassium acid sulphate on gentle heating splits off water, forming a hydrocarbon

¹ Loc. cit.

² Pharm. Arch. 1901, 4, 141, 161.

³ Ber. 1913, 46, 1814.

⁴ J. prakt. Chem. 1894, II, 49, 18.

⁵ 8th Int. Cong. Appl. Chem. 1912, 6, 77.

⁶ Loc. cit.

$C_{15}H_{24}$, boiling at 255 to 257° identical with zingiberene or isozingiberene. Two possible constitutional formulas are given.

Carbohydrates. *Starch*.—See table above.

Pentosans.—Hanus and Bien found 7.64 per cent dry basis. See Introduction to Part III.

TURMERIC

Curcuma longa L. = *Amomum Curcuma* Jacq.

Fr. Curcuma. Sp. Curcuma. It. Curcuma. Ger. Gelbwurz.

Turmeric, a native of India, has long been cultivated in tropical countries for its rhizome, which is valuable as a spice, a drug, and a dyestuff. Several other species of the genus *Curcuma*, including zedoary (*C. Zedoaria* Rose.), round zedoary (*C. aromatica* Salisb.), and mango-ginger (*C. amada* Roxb.), are grown for their pungent, yellow or brown rhizomes, but their use in medicine is rare and in food still more rare. Other species used in starch manufacture are noted under Commercial Starches, Volume I.

As a spice, turmeric is best known as one of the ingredients of curry powder and prepared mustard. It has also been used in adulterated mustard flour and other spices to conceal inferiority.

MACROSCOPIC STRUCTURE.—Two kinds of turmeric are in commerce, the long and the round, known in pharmacy respectively by the Latin, but not botanical, names *C. longa* and *C. rotunda*.

Until Arthur Meyer¹ studied the subterranean system round turmeric was erroneously described as the main or central tuber and long turmeric as the lateral rhizomes, but Meyer found that round turmeric consists of the bulbous, stem-producing organ at the end of a lateral rhizome and long turmeric consists of the rhizomatous branches of round turmeric.

Both forms have transverse rings and root scars, also cut surfaces where the two are separated, and both are scraped, scalded to destroy vitality, and dried. The texture of the flesh is hard, and the color a deep orange.

MICROSCOPIC STRUCTURE.—The histological characters of the fresh rhizomes closely resemble those of ginger except in three details: (1) *bast fibers* are not present in the bundles, (2) the *starch grains* are somewhat different, and (3) the *oleoresin cells*, in addition to volatile oil and resin, contain a deep yellow dyestuff, curcumin.

¹ Arch. Pharm. 1881, 218, 403.

As regards the absence of *bast fibers*, it should be remembered that these occur usually only in the central bundles of ginger.

Authorities differ as to details of form and size of the *starch grains*, their observations doubtless being made on material at different stages of development. This point may be dismissed with the mere statement that the grains are of the ginger type, since they are destroyed by the scalding to which the rhizomes are subjected and exist in the

commercial product as formless lumps impregnated with curcumin.

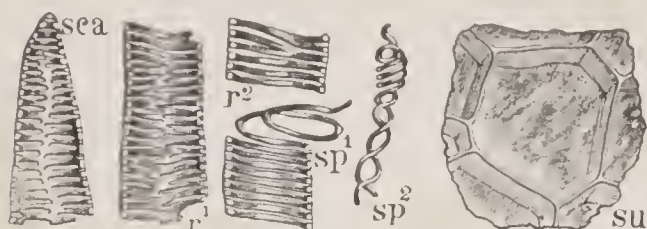


FIG. 36.—Turmeric. Rhizome. *su* cork in surface view. Vessels in longitudinal section: *sca* scalariform, *r*¹, *r*² reticulated, *sp*¹, *sp*² spiral. × 160. (A.L.W.)

Although the diagnostic characters of the starch are lost, the presence of curcumin furnishes a ready means of identification both by chemical and microscopical tests, the simplest being the change in color from yellow to red-brown

with ammonia or sodium hydroxide. Concentrated sulphuric acid produces a crimson color, and naturally iodine in potassium iodide imparts to the starchy lumps the characteristic blue color.

Fig. 36 shows the types of vessels and the cork tissue.

CHIEF STRUCTURAL CHARACTERS.—Rhizomes round or long; flesh of deep orange color.

Microscopic characters like those of ginger except that bast fibers are absent, the starch grains are gelatinized, and curcumin is present. Alkalies impart a red-brown color.

CHEMICAL COMPOSITION.—Proximate analyses of 3 varieties by Leach ¹ show the following composition:

COMPOSITION OF TURMERIC (LEACH)

	Water	Protein	Oil, fixed	Oil, volatile*	Alcohol extract	Starch, crude†	Starch, pure‡	Fiber	Ash, total	Ash, soluble	Sand
	%	%	%	%	%	%	%	%	%	%	%
China.....	9.03	10.81	8.84	2.01	9.22	48.69	40.05	4.45	6.72	5.20	0.11
Pubna....	9.08	6.06	7.60	4.42	7.28	50.08	29.56	5.84	8.52	6.14	
Alleppi....	8.07	9.75	7.51	3.16	4.37	50.44	33.03	5.83	5.99	4.74	
Aver.....	8.73	8.88	7.98	3.19	6.96	49.73	34.21	5.37	7.07	5.36	

* Volatile ether extract. † Reducing matter, after washing with 10% alcohol and direct inversion of residue, calculated as starch. ‡ Diastase method.

¹ J. Am. Chem. Soc. 1904, 26, 1211.

Fixed Oil.—No literature on values and constituents available.

Volatile Oil. *Physical and Chemical Values.*—Gildemeister and Hoffmann¹ give the following values based partly on those reported by Schimmel & Co.² and by Rupe and co-workers:³ specific gravity at 15° C. 0.938 to 0.967, refractive index at 20° C. 1.512 to 1.517, optical rotation -25 to -13° (or $+$ up to $+28^\circ$), acid number 0.6 to 3.1, ester number 6.5 to 16, ester number after acetylation 28 to 53, and soluble in 4 to 5 volumes of 80 per cent alcohol.

Dieterle and Kaiser⁴ describe an oil from *C. domestica* with similar values. Oil of turmeric (*Oleum cinæ*), examined by Rutovskii and Leonov,⁵ appears to be radically different, since its optical rotation was -3.19° and it contained 84.25 per cent of *cineol*. Bacon⁶ examined a Philippine oil, with a yield of 2.4 per cent, having the following values: specific gravity at 30° C. 0.930, refractive index at 30° C. 1.5030, optical rotation $+8.6^\circ$, and ester number 81.

Constituents.—Jackson and Menke⁷ and Jackson and Warren⁸ isolated *turmerol*, an alcohol ($C_{13}H_{18}O$ or $C_{14}H_{20}O$). Rupe and co-workers,⁹ including Luksch,¹⁰ could not obtain pure turmerol or check some of the earlier reactions, but did obtain, by the action of acid or alkali, *curcumone*, a ketone ($C_{12}H_{16}O$) and an isomer of turmerol. Rupe and Wiederkehr¹¹ showed curcumone to have the formula $CH_3 \cdot C_6H_4 \cdot CH(CH_3) \cdot CH_2 \cdot CO \cdot CH_3$. Schimmel & Co.¹² also Rupe,¹² detected *phellandrene*. Luksch showed that the lowest-boiling-point fraction was *d*- α -phellandrene.

The oil of round zeodary (*C. aromatica* Salisb.), examined by Rao, Shintre, and Simonsen¹³ consisted chiefly of sesquiterpenes (*l*-*curcumene*, etc.) and their alcohols, together with small amounts of *d*-camphene and *d*-camphor.

Turmerol boils at 158 to 163° C. (11 to 12 mm.), has a specific gravity at 15° C. of 0.961, and an optical rotation of $+24.58^\circ$.

¹ Ätherischen Öle, Leipzig, 3 Aufl. 1929, 2, 425.

² Rep. Oct. 1894, table p. 44.

³ Ber. 1907, 40, 4909; 1909, 42, 2515; 1911, 44, 584, 1218.

⁴ Arch. Pharm. 1932, 270, 413.

⁵ Troud. Naoutchn. Chim.-Farm. Inst. 1924, No. 10, p. 36.

⁶ Philippine J. Sci. 1910, Sect. A, 5, 257.

⁷ Am. Chem. J. 1882, 4, 368.

⁸ Ibid. 1896, 18, 111.

⁹ Loc. cit.

¹⁰ Inaug. Dis. Basel, 1906.

¹¹ Helv. Chim. Acta 1924, 7, 654.

¹² Loc. cit.

¹³ J. Indian Inst. 1926, 9A, 140.

Carbohydrates. *Starch*.—See table on p. 212.

Pentosans.—Hanus and Bien found 5.57 per cent dry basis. See Introduction to Part III.

Curcumin, $C_{19}H_{12}O_2(OH_2)(OCH_3)_2$, the coloring substance of turmeric, is believed by Iwanof-Gejewsky ¹ to be an alkaloid, although its constitution is not fully understood. It forms yellow or red crystals soluble in alcohol, less so in ether, but insoluble in water, melting at about 180° C. It is light yellow with acids, brown-red with alkalies, and with a solution of boric acid it becomes red, changing to green or blue with alkalies. These tests are commonly carried out on paper impregnated with the color (turmeric paper). The red color with boric acid in dilute solution appears on drying, changing to green or blue on addition of a drop of ammonia water.

¹ Ber. 1870, **3**, 625; 1872, **5**, 1103; 1873, **6**, 196.

STEMS AND LEAVES OF THE LAUREL FAMILY

(*Lauraceæ*)

TREES and shrubs of this family secrete essential oils in their roots, bark, leaves, flowers, and fruits. Sassafras, cinnamon, cassia, and camphor trees are well-known representatives. The avocado (which see) is the fruit of a member of the family. The only leaf of importance in the spice trade is bay leaf.

BAY LEAF

Laurus nobilis L.

Fr. Feuille de laurier. Sp. Laurel. It. Lauro. Ger. Lorbeerblatt.

The specific name of the laurel or bay tree is particularly appropriate as the evergreen leaves were used by the Greeks to crown their victors and today the tree is planted as an ornamental about stately dwellings.

The small tree is a native of the eastern Mediterranean region, but was early introduced into southern Europe. In colder climates it is much grown in tubs.

Although not of first importance as a spice, the dried whole or broken leaves, used with discretion, impart a desirable flavor to pickles, relishes, and meat sauces.

MACROSCOPIC STRUCTURE.—As found on the market, the dried leaves are brown. In a sample at hand, tops with *stem* reaching 9 cm. in length as well as detached leaves are present. The *leaves* are thick, lanceolate, pointed at both ends, often reaching 10 cm. in length, with entire but somewhat revolute edges. On the upper surface they are smooth and lustrous, on the lower surface dull. The *petiole* is short, usually not over 1 cm. long.

MICROSCOPIC STRUCTURE. **Stem.**—The tissues are (1) *epiderm* (Fig. 38, *ep*²) of irregularly thickened cells and numerous sinuous or sickle-shaped hairs with dark contents, (2) *cortex* of thick-walled cells and scattered oleoresin cavities as in the leaf, (3) *bast*

fiber zone, (4) *fibro-vascular bundles* with numerous long and short pitted vessels, also spiral and reticulated vessels, and (5) *pith* of parenchyma with thickened, porous walls.

Petiole.—The *epiderm* (Fig. 38, *ep*¹) consists of longitudinal rows of nearly quadrilateral cells with thickened, often sinuous walls and occasional hairs like those on the stem.

Leaf Blade (Figs. 37 and 38).—The cells of both *epiderms* (*aep*, *iep*) are often elongated in various directions and have thick, porous, sinuous walls. Stomata often occur in pairs. They are lacking in the

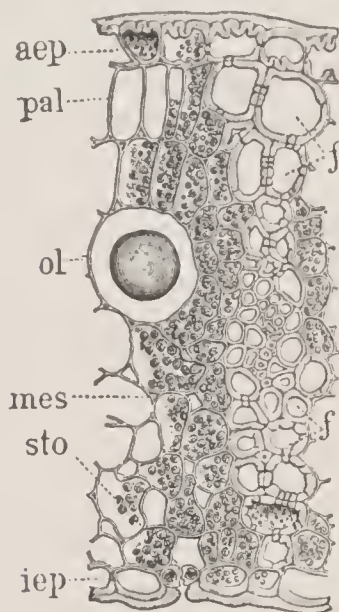


FIG. 37.



FIG. 38.

FIG. 37.—Bay Leaf in cross section. *aep* outer epiderm; *mes* mesophyll with *pal* palisade cells and *ol* oleoresin cavity; *f* fibers of veinlet; *iep* inner epiderm with *sto* stoma. $\times 160$. (K.B.W.)

FIG. 38.—Bay Leaf in surface view. *iep* lower epiderm of leaf blade with stomata occurring singly and in pairs; *ep*¹ epiderm of petiole with hair base; *ep*² epiderm of stem with hairs. $\times 160$. (K.B.W.)

upper epiderm as are also hairs on both epiderms—at least in dried material. Cross sections show that the cuticle of both epiderms is thick and that the outer wall of the upper epiderm is wrinkled.

The *mesophyl* (*mes*) contains oleoresin cavities (*ol*) often with a large drop of volatile oil.

Palisade cells (*pal*) form two rows.

The *fibro-vascular bundle* of the midrib is separated from the epiderms by collenchyma, while those of the veins are separated from the epiderms by thick-walled, porous fibers (*f*) which, seen in cross section, in the case of the smaller veins, form narrow trusses extending through the mesophyl.

CHIEF STRUCTURAL CHARACTERS.—Leaf tapering at both ends, entire with revolute margins, smooth and lustrous above.

Stem and petioles with unicellular, curved hairs. Epiderms of leaf with sinuous, thick-walled cells; stomata in lower epiderm only, often in pairs; mesophyl with oleoresin cavities; fiber-groups of veins extending through mesophyl.

CHEMICAL COMPOSITION.—Analyses of the leaf made at the Münster Experiment Station ¹ gave:

	Water	Protein	Oil, fixed	Oil, volatile	Alcohol extract	N-f. ext.	Fiber	Ash
	%	%	%	%	%	%	%	%
Italian..	9.45	8.34	4.49	3.63	25.01	38.33	31.83	4.53
.....	10.01	10.56	6.19	2.54	23.61	35.55	27.98	4.17

Volatile Oil.—The oil of bay or laurel leaf (*L. nobilis* L.) should not be confused with that from the fruit of the same species or with bay or myrica oil from the leaves of *Pimenta acris* Kost. used for making bay-rum or again with California bay oil from the leaves of *Umbellularia californica* Nutt. By Von Fellenberg's chromic acid oxidation method, Zäch ² obtained 0.8 to 3.0 per cent.

Physical and Chemical Values.—The limits in the following table, although somewhat wide, are in most instances in accord with those of standard treatises such as those of Gildemeister and Hoffmann, Parry, and Allen. Recent figures, obtained by Morani ³ for Italian oil and by Rutovski et al. ⁴ for Crimean, Ssuchum, and Ssotschi oils, are also given.

Country and yield	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Ester No.	Acetyl No. *	Acid No.	Sol. 80% alcohol
All regions:			°				vols.
Min.....	0.910	1.460	−22	20	36	0	1
Max.....	0.945	1.477	− 4	55	98	3	3
Italy (1.28%).....	0.921	1.471	−18	37	84	2	1
Crimea (0.67%)....	0.917	1.471	−16	31	52	1.7
Ssuchum (1.1%)....	0.916	1.464	−18	37	51	0.7
Ssotschi (0.56%)....	0.936	1.468	−18	43	63	0.4

* Ester number after acetylation.

¹ König; Chem. mensh. Nahr.-Genussm., Berlin, 1903, 1, 981.

² Mitt. Lebensm. Hyg. 1932, 23, 156.

³ Ann. chim. appl. 1926, 16, 21.

⁴ Arb. Chem. Pharm. Inst. Moskaus 1925, 11, 59, 93, 118.

Constituents.—Wallach ¹ first reported *cincol* (eucalyptol); Thoms and Molle ² found 50 per cent and Morani ³ 45 per cent. The alcohols include *geraniol* found by Thoms and Molle, *l-linalool* found by Schimmel & Co.,⁴ and in place of *l-linalool*, *l-α-terpineol* found by Morani. Other results by Thoms and Molle are *free eugenol* (this and *methyl eugenol* reported by Schimmel & Co.⁵) 1.7, *combined eugenol* 0.4, *valeric* and *caproic acids* in the ratio of 4 : 6, and an *unnamed acid* (C₁₀H₁₄O₂) 0.07 per cent; other results by Morani are *free alcohols* (terpineol and geraniol) 18, *esters* mostly acetic 13, *aceteugenol* 1.1, *methyl eugenol* 3, *terpenes* 12, and *sesquiterpenes* 3 to 4 per cent. The oil examined by Wallach contained *α-pinene*, but in that examined by Morani this was replaced by the *β-form*. Rotowski and Semijanskaja ⁶ identified *phenylurethan*.

Pentosans.—In dry matter 13.84 per cent. See Hanus and Bien in Introduction to Part III.

¹ Ann. 1889, **252**, 96.

² Arch. Pharm. 1904, **242**, 161.

³ Loc. cit.

⁴ Rep. Apr. 1906, 43.

⁵ Rep. Apr. 1899, 29.

⁶ Riechstoff Ind. 1927, **2**, 218.

LEAVES OF THE MINT FAMILY

(*Labiatae*)

VOLATILE oil, the valuable constituent of this family, is found in surface glands and not as in the parsley family in internal oleoresin passages.

The tribe *Ocimoideæ* is represented by sweet basil; the *Satureineæ*, by peppermint, Japanese mint, water mint, spearmint, marjoram, thyme, and summer savory; and the *Monardeæ*, by rosemary, sage, and clary.

Either the leaves with petioles or in small-leaved species the ends of the leafy stem, including stem and flowers, are gathered and dried for the market.

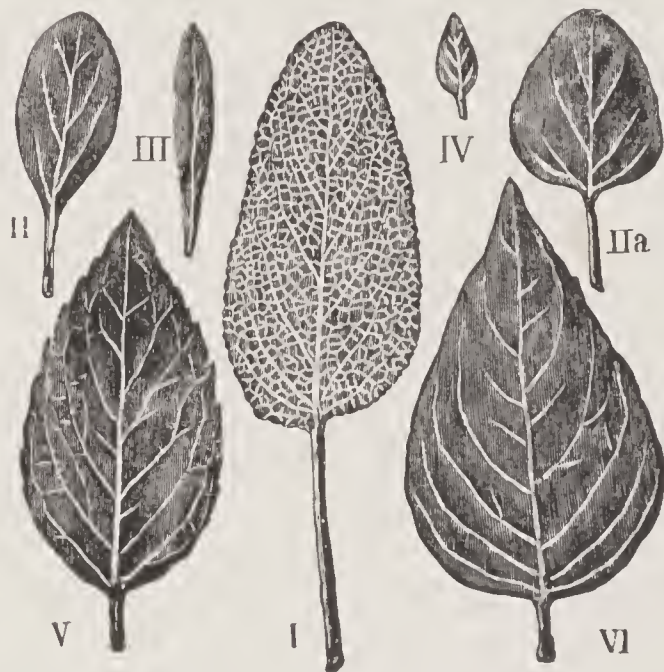


FIG. 39.—Leaves of Pot Herbs. I sage; II sweet marjoram; IIa pot marjoram; III summer savory; IV thyme; V peppermint; VI sweet basil. $\times 1$. (A.L.W.)

The leaves (Fig. 39) of sage, peppermint, spearmint, and basil are relatively large, those of thyme and savory small, and those of sweet and pot marjoram medium. Basil has lustrous leaves which are smooth, except for a few hairs on the lower side of the ribs and petiole; the others are more or less hairy or downy, especially when young. The warty appearance of sage is due to the depression of the veinlets.

COMPARATIVE MICROSCOPIC STRUCTURE. *Stem.*—The bundles of *collenchyma* beneath the epiderm at the four angles contribute rigidity.

Petiole.—The elements noticeable in cross section are (1) *epiderm* similar to that on the veins of the leaves, (2) *collenchyma* of one or more layers, (3) *mesophyl*, (4) *collenchyma* extending along the upper (xylem) and lower (phloem) side of (5) central *fibro-vascular bundle* with fan-shaped rows of vessels.

Arthur Meyer notes the presence of occasional sclerenchyma *fibers* accompanying the collenchyma of large fibro-vascular bundles.

Leaf Blade.—The midrib of well-developed leaves differs from the petiole in that the *collenchyma* when present is interrupted at the sides by mesophyl.

The *epidermal cells* over the veins and veinlets are straight-walled; between the veinlets, especially on the lower side, more or less sinuous. Stomata are most numerous on the lower side. Arthur Meyer notes that when teeth are present *water pores* occur over the ends of the fibro-vascular bundles.

Two general classes of *hairs* occur on all the species: (1) *pointed* and (2) *capitate*. Under each class are unicellular and multicellular or jointed, long and short, warty and smooth, and thick- and thin-walled forms.

Bladder glands form a third class of epidermal outgrowths which, strictly speaking, are hairs with short unicellular stalks and multicellular (usually four to twelve) bladderlike heads. These have been studied among others by Hanstein,¹ Martinet,² Tschirch and Tunmann,³ and Mitlacher.⁴

Tschirch and Tunmann have shown that the volatile oil is secreted in a "resinogenous" lamella of the outer cell wall and is stored in the bladder, formed between the cuticle and the wall proper, which increases in size as the volatile oil accumulates.

Mitlacher illustrates the formation of the cells in the bladder by cell division, the final number being commonly four, eight, and twelve, although Tunmann found as many as twenty in *Hyssopus officinalis* and Martinet thirty-two in *Scutellaria albida*. Illustrations of several well-known authors show the dividing walls of eight-celled heads meeting at the center like spokes of a wheel, which is inconsistent with the laws of cell division.

The following analytical key is based on the characters of the pointed hairs and bladder glands of specimens grown in the writers'

¹ Bot. Ztg. 1868, 21, 697.

² Ann. sci. nat. 1872, [5], 14, 91.

³ Arch. Pharm. 1901, 239, 7.

⁴ Z. allg. oesterr. Apoth.-Ver. 1908, 46, 1.

garden. The distinction between savory and thyme is perhaps too slight to furnish an infallible guide unless corroborated by macroscopic examination.

- I. Hairs branching; glands eight-celled. Rosemary.
- II. Hairs simple (not branching).
 - (1) Hairs short, broad at base; glands four-celled. Sweet basil.
 - (2) Hairs long and short; glands eight- or twelve-celled.
 - (a) Hairs often broad at base, weak; glands mostly twelve-celled. Sweet marjoram.
 - (b) Hairs on midrib and veins only, broad at base, stiff; glands mostly eight-celled. Peppermint.
 - (c) Hairs and glands as in (b) but short hairs between veins also present. Spearmint.
 - (d) Hairs narrow at base, sinuous; glands mostly twelve-celled. Sage.
 - (3) Hairs short; glands twelve-celled.
 - (a) Hairs, glands, and epidermal cells small. Thyme.
 - (b) Hairs, glands, and epidermal cells larger. Summer savory.

COMPARATIVE CHEMICAL COMPOSITION.—The following data on the chief constituents of the volatile oils are tentative. Minor constituents are listed under the individual spices. *Basil*, methyl chavicol the chief constituent, linaloöl next in amount; *peppermint* and *Japanese peppermint*, menthol the chief constituent, menthone present in considerable amount; *water mint*, linaloöl acetate the chief constituent; *spearmint*, carvone the chief constituent; *marjoram*, terpinene and terpineol present; *thyme*, thymol the chief constituent; *savory*, carvacrol the chief constituent; *rosemary*, borneol, pinene, and cineol present; *sage*, borneol and cineol the chief constituents in amount, thujone the chief odorous constituent; *clary*, linaloöl, linalyl acetate, and sclareol present.

SWEET BASIL

Ocimum basilicum L.

Fr. Basilic. Sp. Albahaca. It. Basilico. Ger. Basilienmünze.

Common sweet basil is referred to the above species; the rarer dwarf form is either a mere variety or else a separate species (*O. minimum* L.). Both are garden annuals, natives of tropical Asia and Africa.

MACROSCOPIC STRUCTURE.—Young leaves are distinctly toothed, the teeth becoming indistinct at maturity. Mature leaves (Fig. 39, VI) are ovate, reaching about 5 cm. in length not includ-

ing the petiole of about 2 cm. On the upper surface they are smooth and lustrous; on the lower surface along the midrib and on the petiole, short, stiff hairs occur sparingly.

MICROSCOPIC STRUCTURE (Fig. 40).—Two characters distinguish the leaves from those of other spice leaves of the family: (1) the warty, commonly one- to two-celled, *pointed hairs* with broad bases, and (2) the four-celled *bladder glands*. The *capitate hairs* have commonly a two-celled head with stalk so short as to appear sessile.

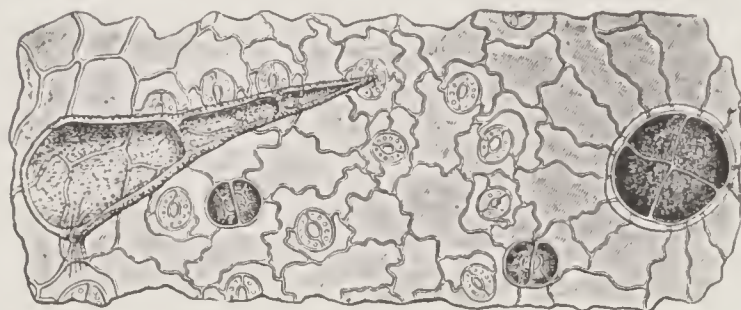


FIG. 40.—Sweet Basil. Lower epiderm of leaf in surface view, showing straight-walled cells, wavy-walled cells, pointed and capitate hairs, and bladder gland. $\times 160$. (A.L.W.)

CHIEF STRUCTURAL CHARACTERS. — Leaves ovate, pointed, blunt toothed when young, smooth above, sparingly hairy below along midrib.

Pointed hairs broad at base, one- to two-celled, faintly warty; capitate hairs with short stalk and two-celled head; bladder glands four-celled.

CHEMICAL COMPOSITION.—Analysis of the herb appears to be confined to yield of oil which reaches on the dry basis about 2 per cent.

Volatile Oil. *Physical and Chemical Values.*—As obtained by distillation in the different regions, the oil varies greatly in composition, probably owing in part to errors in identifying the species. The European oil, known to be true to name, shows according to results of several authors: specific gravity at 15° C. 0.895 to 0.930, refractive index 1.477 to 1.495, optical rotation -22 to -6° , ester number 3 to 15, acid number 0 to 4, and soluble in 1 to 2 parts of 80 per cent alcohol.

Oil from Central Africa, examined by Schimmel & Co.,¹ conforms to these limits, but the inferior product of Réunion and other islands off the East Coast of Africa is higher in specific gravity (up to 0.990) and polarization (up to $+16^{\circ}$). Guenther² gives the following values for Réunion oil: specific gravity at 15° C. 0.945 to 0.987, refractive

¹ Rep. Apr. 1914, 32.

² Am. Perfumer 1935, 30, 183.

index at 20° C. 1.512 to 1.518, optical rotation +0° 22' to +12°, ester number 9 to 22, and acid number up to 3. Roure-Bertrand fils¹ state that oil from Mayotta examined in their laboratory showed: specific gravity at 15° C. 0.970, optical rotation -1°, ester number after acetylation 5.6, acid number 1.4, and soluble in 3 volumes of 80 per cent alcohol. An anonymous author² gives as values for oil from Seychelles: specific gravity at 15° C. 0.962, ester number 2.5, and acid number 0.8. A sample of an Indian oil, examined by Rakshit,³ with an ester number of 178.7, was radically different from that of any species of *Ocimum* here recorded.

Constituents.—French and German oils examined respectively by Dupont and Guerlain⁴ and Bertram and Walbaum⁵ both contained *methyl chavicol* and *linaloöl* and the German oil also *cinol*. Guenther⁶ states that oil from the Grasse region contains about 55 per cent of methyl chavicol and 34.5 to 39.66 per cent of linaloöl. Oil from Réunion of high specific gravity and polarization, as examined by Bertram and Walbaum, contained methyl chavicol, *cinol*, *d-α-pinene*, and *d-camphor*. Van Romburgh⁷ reports the presence of *ocimene*.

Ocimene, C₁₀H₁₆ or CH₂ : CCH₃ · CH₂ · CH₂ · CH : CCH₃ · CH : CH₂, an aliphatic terpene, is prepared from basil oil by the method of Van Romburgh.⁸ Its constitution was determined by Enklaar,⁹ who gives its boiling point under 30 mm. pressure as 81° C. and its refractive index at 18° C. as 1.4857.

CHEMICAL COMPOSITION OF OILS OF OTHER SPECIES.—

O. viride Willd. A sample of oil examined by an anonymous author¹⁰ contained 37 per cent of phenols consisting mostly of thymol. Analyses by Glichitch¹¹ of oils from Grasse and New Caledonia showed the presence of thymol, α- and γ-terpinene, and the following values:

¹ Roure-Bertrand fils Bul. Oct. 1912.

² Bul. Imp. Inst. 1918, 16, 32.

³ Perf. Ess. Oil Rec. 1938, 29, 89.

⁴ Compt. rend. 1897, 124, 300.

⁵ Arch. Pharm. 1897, 235, 176.

⁶ Loc. cit.

⁷ Verlag lands Plant. Buitenzorg 1898, 28; 1899, 48; 1901, 58.

⁸ Loc. cit.

⁹ Rec. trav. chim. 1907, 26, 157; 1908, 27, 422; 1917, 36, 215; 1926, 45, 337; Ber. 1908, 41, 2083.

¹⁰ Bul. Imp. Inst. 1920, 18, 348.

¹¹ Bul. soc. chim. 1923, 33, 1536.

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Ester No.	Formyl No.*	Esters†	Alco- hols, total‡	Alco- hols, com- bined‡	Alco- hols, free‡	Phe- nols§	Sol. 80% alcohol
			°			%	%	%	%	%	vols.
Grasse	0.910	1.4969	+0.9	5.6	112	1.96	32.53	1.54	30.99	38	1.5
N. C.	0.930	1.4952	+1.5	2.1	91.6	0.73	26.34	0.58	25.76	18

* Ester number after formylation. † As linaloöl acetate. ‡ As linaloöl. § Largely or entirely thymol.

O. canum Sims = *O. americanum* L. The oil from the fruit,¹ with a specific gravity at 15° C. of 0.953 and polarizing at 24° C. +2.75°, contained no appreciable amount of thymol or any phenol. Two oils said to be from this species, but whether from the fruit or leaves is uncertain, examined by Chiris,² differed in that one was high in methyl cinnamate, the other in *d*-camphor. Glichitch³ found in one of these samples: methyl cinnamate and allocinnamate 55, free *l*-linaloöl 25, estragol 2, eucalyptol 1, geraniol 0.5, other alcohols 1, aliphatic esters (6 to 8 carbons) 0.5, *l*-sesquiterpene 10, and *d*-sesquiterpene 4 per cent.

O. gratissimum L. An oil from the leaves of this species contained, as reported by Roberts,⁴ phenols (chiefly eugenol) 55, phenyl ethers (calculated as methyl chavicol) 5.6, alcohols (calculated as linaloöl) 13, esters (calculated as linaloöl) 0.6, terpenes (chiefly ocimene) 16, and other matters 9.8 per cent.

O. sanctum L. Two oils of this species,⁵ with specific gravity at 15.5° C. 0.9840, refractive index at 20° C. 1.5210, and optical rotation at 20° C. -29.37°, contained 33 per cent of phenols consisting largely of eugenol (first reference) or chavibetol (second reference).

PEPPERMINT

Mentha piperita L.

Fr. Menthe poivrée. Sp. *Mentha piperita*. It. *Mentha peperita*.
Ger. Pfefferminze.

Peppermint, a plant of European origin, is the most commonly grown of all the mints. While the leaves are used occasionally in the kitchen and for preparing sugared leaves, it is the oil prepared

¹ Bul. Imp. Inst. 1924, 22, 265.

² Parf. France 1924, No. 20, 290.

³ Ibid. 1924, No. 21, 314.

⁴ J. Soc. Chem. Ind. 1921, 40, 164.

⁵ Bul. Imp. Inst. 1934, 32, 511; 1937, 35, 298.

from them on a commercial scale that is most used for flavoring confectionery, chewing gum, jellies, carbonated beverages, and cordials.

The variety grown at Mitcham, Surrey, England, has been introduced into continental Europe, Japan, and America.

MACROSCOPIC STRUCTURE (Fig. 39, V).—Although varying greatly, the *leaves* are commonly up to 5 cm. long, ovate or oblong, pointed, and irregularly serrate, longer and shorter teeth often alternating. The *petiole* in large leaves reaches 1 cm. in length.

Hairs occur in appreciable numbers only on the lower surface of the midrib and larger veins, while in the case of spearmint (*M. spicata* L.) short hairs occur between the veins. Leaves of *M. silvestris* L. have a dense felt of soft hairs on the under surface, and those of *M. arvensis* L. are more hairy on the midrib, veins, and margins than peppermint.

Varieties of the above and other species, as well as hybrids, with curled leaves, loosely designated *M. crispa*, also Japanese mint, a variety of *M. arvensis* L. with various Latin varietal names, yield commercial peppermint oil inferior to that distilled from true peppermint.

Tschirch and Oesterle¹ lay stress on the form of the teeth and the venation into the teeth as means of distinguishing peppermint from other species.

MICROSCOPIC STRUCTURE.—**Stem, Petiole, and Midrib** are strongly developed. *Collenchyma* occurs in the stem at the angles, also in the petiole and midrib beneath both epiderms and adjoining the xylem and phloem of the large fanlike fibro-vascular bundle.

Leaf Blade.—The *pointed hairs* on the veins and veinlets are short, warty, commonly one- to two-celled (Fig. 41, I). On the midrib and petiole long (up to 1 mm.), several-jointed, pointed, thick-walled, *warty hairs* occur sparingly (Fig. 41, II). *Capitate hairs*, with very

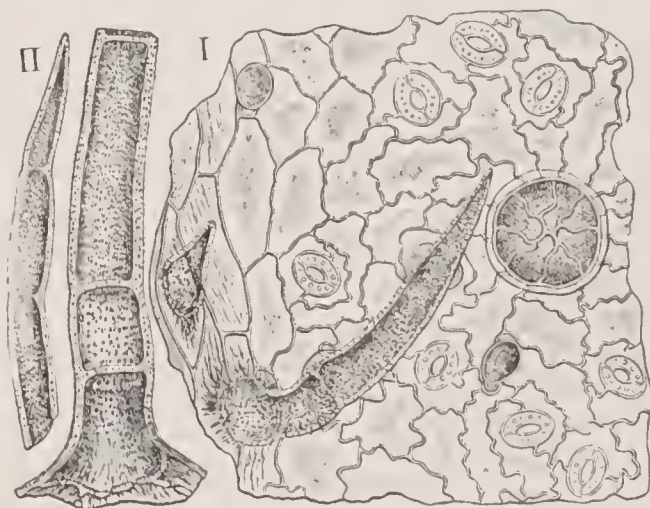


FIG. 41.—Peppermint. Lower epiderm of leaf in surface view. I straight-walled cells, wavy-walled cells, pointed and capitate hairs, and bladder gland. II hair 0.8 mm. long from midrib. $\times 160$. (A.L.W.)

¹ Anat. Atlas, Leipzig 1900, Taf. 19.

short, unicellular stem and oval head, and *bladder glands*, with eight cells, are distributed over both *epiderms*.

Crystals of *menthol* may often be seen in the bladder glands of glycerin mounts of dry or fresh leaves. They dissolve in alcohol, ether, and chloroform. Crystal groups of *hesperidin* are numerous in the epidermal cells.

A single *palisade layer* underlies the upper epiderm.

CHIEF STRUCTURAL CHARACTERS.—Leaves visibly hairy on midrib and larger veins of lower surface.

Hairs (1) pointed, warty, mostly short, one- to two-celled, on midrib long, up to eight-celled; (2) capitate with short one-celled stem. Bladder glands eight-celled.

CHEMICAL COMPOSITION. Peppermint Oil.—The literature of peppermint oil is more extensive than that of any other volatile oil used in foods, and the botanical sources of some of the samples described therein are uncertain. The yield varies up to 0.25 per cent.

Physical and Chemical Values.—The following authors, publishing with one exception since 1900, have reported values of the oil produced in different countries: *Australia*, Schimmel & Co.;¹ *British East Africa*, Schimmel & Co.;² *Caucasus*, Maisit;³ *England*, Schimmel & Co.;⁴ *Esthonia*, Weiderpass;⁵ *France*, Schimmel & Co.,⁶ Fondard and Autran,⁷ Pipert;⁸ *Germany*, Mohlk,⁹ Haensel,¹⁰ Burger;¹¹ *Hungary*, Janicsek;¹² *Ireland*, Reilly and Taylor;¹³ *Italy*, Zay,¹⁴ Fenaroli;¹⁵ *Japan* (English and German origin), Shinosaki;¹⁶ *Palestine*, Schimmel & Co.;¹⁷ *Russia*, Schimmel & Co.,¹⁸ Pigulevskii,¹⁹ Rutovskii, Vinogra-

¹ Rep. 1927, 83.

² Rep. Oct. 1915, 32.

³ Arch. Pharm. 1911, **249**, 637.

⁴ Rep. 1927, 83.

⁵ Acta et Comm. Dorpat 1924, A. V. 11 pp.

⁶ Rep. Apr. 1905, 62; 1927, 83.

⁷ Parf. Francee 1925, **23**, 10.

⁸ Perf. Ess. Oil Rec. 1926, **17**, 170.

⁹ Arch. Pharm. Chem. 1915, **22**, 128, 189, 241.

¹⁰ Chem. Zentr. 1911, I, 1839.

¹¹ Riechstoff Ind. 1932, **7**, 147.

¹² Mezőgazdasági Kutatások 1929, **2**, 153; Kísérletügyi Közlemények 1934, **37**, 147.

¹³ Perf. Ess. Oil Rec. 1926, **17**, 469.

¹⁴ Staz. sper. agr. ital. 1902, **35**, 816.

¹⁵ Riv. ital. ess. prof. 1930, **12**, 187.

¹⁶ J. Ind. Eng. Chem. 1913, **8**, 658.

¹⁷ Rep. 1927, 80.

¹⁸ Rep. Apr. 1907, 82; Oct. 1915, 32.

¹⁹ J. Russ. Phys.-Chem. Soc. 1920, **51**, I, 60.

dova, and Kondratskii,¹ Sobolevskaya;² *United States*, Power and Kleber,³ (Pacific Coast), Johnson and Wilkes,⁴ Lazell.⁵ Earlier work is reviewed in the works of Allen, Parry, and Gildemeister and Hoffmann.

In reporting the values of peppermint oil, it is customary to express the results on saponification before and after acetylation in terms of free, combined, and total menthol, rather than ester number and acetyl number (ester number after acetylation). This is because the content of menthol, the chief and most valuable constituent, is the basis of commercial valuations.

Gildemeister and Hoffmann⁶ classify the range in values for peppermint oil according to countries.

In the following table are given the limits for the oils of all countries except Japan as found by all the authors whose figures are available and for 23 English, 50 American, and 6 Kenya oils as recently reported by Parry and Ferguson.⁷ It is noteworthy that, although

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Menthol, total	Menthol, free	Menthol, com- bined	Men- thone	Sol. 70% alcohol
			°	%	%	%	%	vol.
All authors:								
Min.	0.900	1.457	−35	34	24	2*	8	3
Max.	0.930†	1.472	− 5	86	61	30*	42	5
P. and F.:								
English								
Min. . . .	0.9022	1.4591	−32	42.4	2.3‡	22.6
Max. . . .	0.9144	1.4643	−23	64.9	10.1‡	42.1
American								
Min. . . .	0.9027	1.4600	−31	46.8	4.5‡	16.9
Max. . . .	0.9245	1.4680	−19	61.7	11.0‡	30.8
Kenya								
Min. . . .	0.9229	1.4603	−21	52.7	24.1‡	10.6
Max. . . .	0.9243	1.4621	−12	60.3	33.3‡	12.7

* Calculated as menthol. † Johnson and Wilkes: 0.950. ‡ Esters calculated as menthyl acetate. Results about one-third higher than when calculated as menthol.

¹ Arb. Chem. Pharmaz. Inst. Moskaus 1925, **11**, 59.

² Trans. Sci. Chem.-Pharm. Inst. Moskaus 1928, **19**, 186 (German p. 194.)

³ Arch. Pharm. 1894, **232**, 639.

⁴ J. Am. Pharm. Ass. 1923, **12**, 782.

⁵ Perf. Ess. Oil Rec. 1928, **19**, 183.

⁶ Ätherischen Öle, Leipzig, 3 Aufl. 1931, **3**, 786.

⁷ Chem. & Drug. 1936, **124**, 37.

the figures on physical values of the latter authors are within those of earlier investigators, the maximum for menthol is lower (64.9 instead of 86) and for menthone is higher (42.1 instead of 18 per cent).

The *U. S. Standards* require that oil of peppermint contain not less than 50 per cent by weight of menthol and that peppermint extract contain not less than 3 per cent by volume of peppermint oil.

The following interesting results are by Charabot: ¹

	Sp. gr.	Opt. rot.	Free menthol	Menthyl acetate	Methone
		°	%	%	%
Before budding.....	0.9025	−25° 10′	44.3	3.7	5.2
Budded, leaves.....	0.9016	−26°	42.2	10.3	4.2
Budded, buds.....	0.9081	−20° 15′	29.9	7.5	16.7
Flowering plant.....	0.9200	− 2° 37′	32.1	10.7	10 2

In experiments conducted by Chiris ² the maximum yield in percentage of oil was obtained immediately before the rapid growth preceding flowering, but the maximum yield per acre was just before or during early bloom. The percentage of menthol, free and combined, also the specific gravity and rotation increased suddenly after the falling of the blossoms.

Figures obtained by Sardanovskii ³ show that stems over a year old, especially before blooming, are deficient in oil, the leaves, however, are richest in oil just before blooming. The menthol content is highest at the end of blooming; the ester content increases during bud formation, decreases during blooming, and increases thereafter. Withering causes a decrease in yield but an increase in menthol and esters.

Mikhalov ⁴ observed a direct relation between mean temperature and yield of oil. Thus in July the yield was 2 per cent, in October only 0.6 per cent. Age of the leaves is a minor factor.

Constituents.—As indicated in the above table, *l-menthol*, a secondary alcohol, chiefly in the free state, is the principal constituent and *l-menthone*, a ketone formed by the oxidation of menthol, is present in large amount.

The extensive investigation of American oils by Power and Kleber ⁵

¹ Compt. rend. 1900, **130**, 518.

² Parf. France 1925, **28**, 151.

³ Farm. Zhurn. 1929, 18.

⁴ Masloboino Zhirovoc Delo 1929, No. 11, 63.

⁵ Loc. cit.

disclosed the following minor constituents: *acetic* and *isovaleric acids*, also their aldehydes and menthyl esters; a *menthyl ester* of an unidentified acid ($C_8H_{12}O_2$); *lactone*; the diterpenes ($C_{10}H_{16}$) *phellandrene*, *i-pinene*, *l-limonene*; the sesquiterpene *cadinene* ($C_{15}H_{24}$); and *cineol* ($C_{10}H_{18}O$). *Menthene* ($C_{10}H_{16}$), stated by Andrees and Andrees¹ and Schindelmeiser² to be present in Russian oil, was not found. Schimmel & Co.³ detected *amyl alcohol* and *dimethyl sulphide*. Kremers,⁴ in addition to confirming the presence of *l-menthol*, *l-menthone*, and *cineol*, identified *pulegone* and *d-piperitone* ($C_{10}H_{16}O$), a menthenone (Δ^1) closely resembling *pulegone*. He⁵ found that *isovaleraldehyde* was the aldehyde present in greatest amount. In American oil, Gordon⁶ identified *terpinene* and *d-menthone*.

The occurrence of *dimenthyl sulphide* was brought out by Schimmel & Co.⁷

Carles⁸ isolated from a profusely flowering crop of the Mitcham strain, grown during a dry season in Italy, a new oxygenated constituent with the odor of mint blossoms that gave stronger reactions with the various tests differentiating Japanese and common oils than the oils themselves. The partially purified substance obtained by repeated fractionation showed: specific gravity at 15° C. 0.965, refractive index at 20° C. 1.4807, optical rotation +81°, and boiling point under 20 mm. 95° C.

Wasicky⁹ reports a yield in *M. piperita austriaca* of 1.8 to 1.9 per cent of oil containing 56 per cent of free menthol and 4 per cent of esters.

l-Menthol or methylisopropylhexahydrophenol, $C_{10}H_{20}O$ or $C_6H_9(CH_3)(OH)(C_3H_7)$ (see structural formula in Introduction to Spices), a secondary alcohol with only single bonds in the ring, is the constituent of peppermint oil that gives it its cooling taste and characteristic odor. It is conveniently prepared from Japanese peppermint oil by removing and purifying the crystals which separate out at ordinary temperature. The lustrous hexagonal prisms melt at 43° and boil at 212° C.

¹ Ber. 1892, 25, 609.

² Apoth. Ztg. 1907, 21, 927.

³ Rep. Oct. 1894, 41; Oct. 1896, 58.

⁴ J. Biol. Chem. 1922, 52, 443; Am. J. Pharm. 1925, 97, 658.

⁵ Am. J. Pharm. 1926, 98, 86.

⁶ Ibid. 1927, 99, 523; J. Am. Pharm. Ass. 1927, 16, 13.

⁷ Rep. Apr. 1909, 55.

⁸ Parf. mod. 1929, 22, 615.

⁹ Scientia Pharm. 1937, 8, 33.

Menthone, $C_{10}H_{18}O$ or $C_6H_8(CH_3)(O)(C_3H_7)$, is a liquid ketone, the relationship to menthol being evident from the formula. One may be converted into the other. Leser¹ and Haller² have synthesized menthone from isopropyl iodide. The substance has a specific gravity at 20° C. of 0.896 and boils at 206° C. Right and left polarizing modifications have been isolated.

Tests for Japanese Peppermint Oil.—Eaton³ has combined and modified the U. S. Pharmacopœia color tests, employing 5 drops of the oil, 1 cc. of glacial acetic acid, and 1 drop of concentrated nitric acid in a small test tube. On heating on a water bath to about 60° C. for 1 to 2 minutes oil from *M. piperita* takes on a color which is violet or blue by transmitted light and fluorescent copper-colored by reflected light, whereas Japanese peppermint oil gives a straw color with sometimes a faint blue, but not the fluorescence.

Attention has been called by Garratt⁴ to the presence in Japanese peppermint oil of furfural which causes a red coloration when a mixture of 0.1 cc. of the oil with 5 cc. of a 2 per cent solution of freshly distilled aniline in glacial acetic acid is allowed to stand 10 minutes in the dark. Examined in the Lovibond tintometer, red values of 4.5 to 7.3 were obtained for Japanese oils, but only about 0.7 for American oils.

Terpeneless Peppermint Oil has the advantage over the ordinary oil in that it dissolves without cloudiness in dilute alcohol. Haensel⁵ gives the following values for specific gravity at 15° C. and optical rotation respectively: English (Mitcham) 0.9082, -28.8° ; French 0.9240, -13.0° ; American 0.9120, -19.5° ; Japanese 0.9060, -24.2° .

Non-Volatile Constituents found in the leaf by Braun⁶ include: ash 6.77, water-insoluble ash 5.10, and pentosans 6.28 per cent; also a hydrocarbon ($C_{31}H_{64}$) melting at 69° C.; a phytosterol melting at 134 to 135° C.; phytosterolin, melting at 279° C.; glycerol; palmitic, stearic, oleic, melissic, and linolenic acids; an acid ($C_{18}H_{36}O_2$) melting at 100 to 101° C.; hesperetin melting at 225° C.; hesperidin melting at 250 to 251° C.; rhamnose; dextrose; and betaine. The stems contained: ash 15.33 and water-insoluble ash 9.23 per cent.

¹ Compt. rend. 1902, **134**, 1115.

² Ibid. 1905, **140**, 127.

³ J. Ass. Off. Agr. Chem. 1922, **5**, 597.

⁴ Analyst 1935, **60**, 369.

⁵ Apoth. Ztg. 1907, **22**, 274.

⁶ Ibid. 1930, **102**, 202.

CHEMICAL COMPOSITION OF OILS OF OTHER SPECIES.—The chief constituents of oils of various species of *Mentha* are of interest compared with those of peppermint (largely menthol), Japanese peppermint (containing menthenone), spearmint (chief constituent carvone and characteristic constituent dihydrocarveol), and water mint (largely linaloöl acetate).

Pennyroyal (*M. Pulegium* L.) contains *pulegone* as the chief constituent while the variety *hirsuta* Guss. contains *piperitone* instead of pulegone, according to Pellini.¹ American wild mint (*M. canadensis* L.), according to Kremers,² yields over 2 per cent of oil containing 90 per cent of *pulegone*. Bergamot mint (*M. citrata* Ehrh.) grown in Michigan contains an oil showing 57.5 per cent of esters of *linalyl acetate* and 14.6 per cent of alcohols as *linaloöl*.³ A Mediterranean mint (*M. mirennæ* Mir.) furnishes an oil containing, as examined by Bruno,⁴ 13.78 per cent of *menthol* and 42.18 per cent of *linaloöl*; Rovesti and Rovesti⁵ secured similar results.

JAPANESE PEPPERMINT

Mentha arvensis var. *piperascens* Malinvaud.

This species grows not only in Japan but also in China and Korea.

Japanese Peppermint Oil, at ordinary temperatures, is characterized by the presence of menthol crystals distributed through the thick oily liquid. It is inferior in flavor to common peppermint oil, but is high in menthol, thus being adapted for the manufacture of commercial menthol. The partially dementholized oil is also marketed. This contains correspondingly higher percentages of menthone.

Physical and Chemical Values.—The following limits take account of early work and more recent analyses by Thoms,⁶ Murayama,⁷ Umney,⁸ Shinozaki,⁹ and Nakao and Shibue:¹⁰

¹ Ann. chim. appl. 1923, **13**, 97.

² J. Am. Pharm. Ass. 1925, **14**, 32.

³ Parf. Mod. 1925, **18**, 205.

⁴ Riv. ital. ess. 1925, **7**, 67.

⁵ Prof. ital. 1926, **4**, 384.

⁶ Ber. deutsch. pharm. Ges. 1910, **20**, 424.

⁷ Schimmel & Co. Rep. Apr. 1912, 103.

⁸ Perf. Ess. Oil Rec. 1913, **4**, 32.

⁹ J. Ind. Eng. Chem. 1913, **5**, 658; J. Chem. Ind. Japan 1919, **22**, 296, 349, 458.

¹⁰ J. Pharm. Soc. Japan 1923, **499**, 726.

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Solid. point	Menthol, total	Menthol, free	Menthol, com- bined	Men- thone	Sol. 80% alcohol
Min..	0.890	1.4600	°	°C.	%	%	%	%	vols.
Max.	0.919	1.4645†	—55	+17	70	58*	2	11	2.5
			—30	+28	92	85	10*	14	5

* Oil from old discarded leaves contained 29.0% of free and 39% as esters (N. and S.).

† Up to 1.6607 in Shinozaki's first paper.

Four samples of oil from plants grown in 1934, 1935, and 1936 in Hungary gave results by Rom¹ as follows: yield 0.26 to 1.60 per cent, melting point of crystals 14 to 16° C., specific gravity 0.8951 to 0.9029, refractive index at 20° C. 1.4590 to 1.4618, optical rotation —40.5 to —37.5°, iodine number 44.2 to 48.6, solubility in 70 per cent alcohol 2.6 to 2.8, menthyl esters 4.8 to 8.0 per cent, and total menthol 81.1 to 83.4 per cent.

Constituents.—A list of the chief constituents of Japanese oil by Shinozaki and Nagasawa² includes *l*-menthol, ethylamylcarbinol, β,γ -hexenol, menthone, *i*- and *d*-isomenthone, menthenone, *l*-limonene, α -pinene, camphene, and various acids free and combined. Of these menthenone had been isolated by Schimmel & Co.,³ limonene by Murayama,⁴ and β,γ -hexenol by Walbaum and Rosenthal,⁵ who also found α,β -hexenic acid. In the fraction boiling above 240° C., Shinozaki and Nagazawa⁶ identified *l*-menthol, menthol, *l*-menthone, sesquiterpene, *dl*-sesquiterpene alcohol, and the following acids, free or combined: *formic*, *acetic*, *isovaleric*, and *caproic*. Duncan and Short⁷ give limonene and α -pinene as the principal terpenes and *caryophyllene* as the principal sesquiterpene. A trace of an unidentified *d*-sesquiterpene was also reported.

Menthenone, C₁₀H₁₆O, is a ketone peculiar to the species: specific gravity at 15° C. 0.9382, refractive index at 20° C. 1.4844, optical rotation 1.5°, boiling point at 752 mm. 235 to 237° C., and molecular refraction 46.58. It is prepared by decomposition of the sulphite.

¹ Pharm. Monatsh. 1937, **18**, 6.

² Rep. Imp. Ind. Res. Inst. Osaka 1929, **10**, No. 5.

³ Rep. Oct. 1910, 96.

⁴ J. Pharm. Soc. Japan, 1910, No. **307**, 141.

⁵ Schimmel & Co. Ber. 1929, 205.

⁶ Rep. Osaka Ind. Res. Lab. Japan 1930, **11**, Nos. 9 and 10.

⁷ J. Soc. Chem. Ind. 1931, **50**, 198T.

Shinozaki, Nagasawa, and Makino,¹ in their studies of substances yielding addition products with alkali sulphites, decided that menthenone was the most abundant constituent of the high-boiling fraction. These sulphite-reacting compounds form about 10 per cent of the oil produced in the Hokkaido district.

Dementholized Japanese Peppermint Oil.—The oil examined by Tanaka² showed as follows: specific gravity at 25° C. 0.8957, refractive index at 25° C. 1.4063, optical rotation -30.7° , saponification number 25.4, saponification number after esterification 142.4, saponification number of hydrogenated oil after esterification 229.1, and acid number 1.2. The following constituents were also found: *l*-menthol 37.3, *l*-menthyl acetate 8.5, total ketones (*l*-menthone 32.3, piperitone 1.3) 33.6, total hydrocarbons (*p*-menthene 1.5, *l*-limonene 9.8) 12.6, isovaleric acid 0.3 per cent, and amylethylcarbinol and isovaleric aldehyde traces.

The dementholized oils of Rom³ had the following values: specific gravity 0.8876 to 0.8977, refractive index at 20° C. 1.4600 to 1.4620, optical rotation -30.0 to -25.0° , solubility in 70 per cent alcohol 3.0 to 3.3; they contained menthyl esters 7.7 to 13.2 and total menthol 46.8 to 52.2 per cent.

WATER MINT

Mentha aquatica L.

Fr. Menthe crépue. Ger. Wassermintze.

This species is a native of Europe, where it is cultivated, and, introduced, occurs sparingly in the United States.

Water Mint Oil resembles peppermint oil in odor.

Physical and Chemical Values.—The following values are according to Rutovskii et al.⁴ and Chernukhin⁵: specific gravity at 15° C. 0.9626, refractive index 1.4865, optical rotation $+28.2^\circ$, ester number 47.4, and ester number after acetylation 91.5. A sample examined thirty-four years earlier by Schimmel & Co.⁶ had a specific gravity at 15° C. of 0.880 and an optical rotation of $-2^\circ 14'$.

¹ Rep. Imp. Ind. Res. Inst. Osaka 1927, 7, No. 1.

² J. Chem. Soc. Japan 1929, 50, 546.

³ Loc. cit.

⁴ Perf. Ess. Oil Rec. 1928, 19, 391.

⁵ Trans. Sci. Chem.-Pharm. Inst. Moscow 1928, 19, 196; in English p. 201.

⁶ Rep. Oct. 1894, table p. 46.

Masino¹ obtained by steam distillation of the plant before flowering and ether extraction of the distillate 0.8 per cent of volatile oil with a specific gravity at 14° C. of 0.867 and an optical rotation of -0.41° .

Constituents.—Kremers² states that the oil consists largely of *linaloöl acetate* with smaller amounts of another *ester*, *linaloöl*, a *free acid*, and an unstable *aldehyde*.

Gordon,³ on distillation of an alcoholic extract of partly dried leaves stripped from the branches, secured an oil which gave a strong reaction for furfural and certain sesquiterpenes and had the following values: specific gravity at 21°/21° C. 0.8649, refractive index at 25° C. 1.4588, optical rotation at 25° C. $+2.54^{\circ}$, ester number 39.79, ester number after acetylation 120.5, esters as *linaloöl acetate* 13.93 per cent, total alcohol 47.38 per cent, and free alcohol as *linaloöl* 36.43 per cent. The aqueous distillate contained *acetic acid* and *trimethylamine*.

Non-Volatile Constituents.—In the residue after distillation the following were found by Gordon⁴: *potassium nitrate*; *ammonium chloride*; *formic*, *succinic*, *linolenic*, *linolic*, *oleic*, *melissic*, *myristic*, *palmitic*, *stearic* (?), *butyric* (?), *hexylic* (?), and *heptylic* (?) *acids*; *dextrose*; *rhamnose*; *betaine*; *choline*; *methylamine*; *linaloöl*; *dotriacontane*; a *phytosterol*, *lupeol*; *aquaticol*; and other substances not identified.

SPEARMINT

Mentha spicata L. = *M. viridis* L.

Fr. Menthe verte. Sp. Menta. It. Menta verte. Ger. Krauseminze.

Spearmint, a native of the Old World, is grown on a considerable scale in Michigan and New York for the production of spearmint oil, which has come into prominence as a flavor for cordials, chewing gum, and confectionery. A limited amount of the leaf is used for preparing mint sauce, mint julep, and candied spearmint.

MACROSCOPIC STRUCTURE.—Although commonly stated to be glabrous, the *stem* and *leaves* are more hairy than those of peppermint. It further differs in being green throughout, whereas peppermint often has reddish purple stem and petioles. Both species have short petioles. Distinctions based on the serration are of uncertain value.

¹ Bol. chim.-farm. 1936, **75**, 390, 393.

² J. Biol. Chem. 1922, **52**, 439.

³ Am. J. Pharm. 1928, **100**, 433, 509.

⁴ Loc. cit.

The odor to one familiar with the two species is unmistakable and the best means of distinction.

MICROSCOPIC STRUCTURE. Leaf Blade.—In addition to long, jointed, warty, *pointed* hairs occurring on the midrib and veins as in peppermint, there are also distributed over the whole lower surface and near the margins of the upper side numerous short, mostly unicellular, *warty hairs*, often no longer than broad. Eight-celled *bladder glands* and *capitate hairs* occur on both surfaces as in peppermint.

CHIEF STRUCTURAL CHARACTERS.—Leaves green, petioled, more hairy than those of peppermint, of characteristic odor.

Hairs and bladder glands as in peppermint, but short, mostly unicellular, pointed hairs occur between veins.

CHEMICAL COMPOSITION.—**Spearmint Oil** is distilled with steam from both European and American plants, the yield of the fresh leaves varying up to 0.3 per cent. Germany and Hungary are large producers. The oil of water mint (*M. aquatica* L.), which has a similar flavor, is sometimes substituted for the true oil.

Physical and Chemical Values.—In preparing the following table, account was taken of the figures secured by Schimmel & Co.¹ on Hungarian and other European oils, by Dorronsora ² on Spanish oils, by Rovesti ³ and by Bonaccorsi ⁴ on Italian oils, by Holmes ⁵ on New Jersey oil, by Nelson ⁶ on Michigan oils, and by Christensen and Hiner ⁷ on Florida oils, also those by Gildemeister and Hoffmann:

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Ester No.	Acid No.	Ketones (carvone, etc.)	Sol. 80% alcohol
			°			%	vols.
Min.	0.883	1.4800	−59	18	0	43	1
Max.	0.947*	1.4970	−30	36	2	80	1.5

* Rarely up to 0.980.

The *U. S. Standards* require that spearmint extract contain not less than 3 per cent by volume of oil of spearmint.

¹ Rep. Oct. 1894, table p. 40.; Oct. 1896, 45; Apr. 1897, 49; Apr. 1909, 55.
² Mem. real. acad. cienc. Madrid 1919, 29.
³ Prof. ital. 1925, 3, 180.
⁴ Bol. uffic. staz. sper. ind. essenze e deriv. agrumi 1935, 10, 159.
⁵ Perf. Ess. Oil Rec. 1911, 2, 197.
⁶ U. S. Dept. Agr., Bur. Chem. 1912, Circ. 92.
⁷ J. Am. Pharm. Ass. 1932 21, 147.

Christensen and Hiner,¹ who found in Florida oil optical rotation at 25° C. -56.09 to -59.08° and carvone 69.5 to 80.2 per cent, recommend -59 to -48° as an allowed range of the former and 50 per cent minimum for the latter.

So-called spearmint oil distilled from the dried leaves of *M. longifolia* Huds., examined at the Imperial Institute,² showed: specific gravity at 15° C. 0.947, refractive index 1.4925, optical rotation -47.6° , and ketones (largely carvone) 70 per cent.

Constituents.—*l*-Carvone, first noted by Gladstone,³ forms the greater part of the oil, the amount found by Kremers and Schreiner⁴ reaching 56 per cent and by Nelson⁵ 66 per cent, but the constituent contributing the characteristic flavor is a minor one considered by Elze⁶ to be *dihydrocuminic alcohol* (18 per cent calculated as acetate) and by Nelson to be *dihydrocarveol* both free and combined. Nelson was unable to find dihydrocuminyl alcohol in American oils, but did find *limonene* and a small amount of *l*-phellandrene, also *acetic acid* and its homologs. Haensel⁷ in German oil detected *dipentene* and *cineol*, and Bonaccorsi⁸ in Calabrian oil α -*pinene*. Schimmel & Co.⁹ showed that Russian oil contained cineol but otherwise was of radically different composition, containing 50 to 60 per cent of *l*-linaloöl and only 5 to 10 per cent of carvone.

Carvone.—See Caraway.

Dihydrocarveol, $C_{10}H_{18}O$ or $C_6H_9(CH_3)(OH)(C_3H_5)$, is a liquid formed by the reduction of carvone in an alcoholic solution. It boils at 224° C.

SWEET MARJORAM

Origanum Majorana L. = *Majorana hortensis* Moench.

Fr. Marjolaine. Sp. Meiorana. It. Maiorana. Ger. Majoran.

In the spice trade the term marjoram is applied to the leaves of sweet marjoram, a native of the Mediterranean region and western Asia. Although a perennial, it is commonly grown as an annual.

Pot marjoram (*O. vulgare* L.) is grown as a perennial in the kitchen garden.

MACROSCOPIC STRUCTURE (Fig. 39, II).—Sweet marjoram has a spatulate leaf narrowed into a petiole. The leaf blade reaches about

¹ Loc. cit.

² Bul. 1920, 18, 350.

³ J. Chem. Soc. 1872, 25, 1.

⁴ Pharm. Rev. 1896, 14, 244.

⁵ Loc. cit.

⁶ Chem Ztg. 1910, 34, 1175.

⁷ Chem. Zentr. 1907, 1, 1332.

⁸ Loc. cit.

⁹ Rep. Apr 1898, 46.

2 cm. in length and 1 cm. in breadth. Three to five distinct veins occur on each side of the midrib. Both surfaces, the petiole, and the stem are downy-hairy. Pot marjoram (Fig. 39, IIa) has a broadly ovate leaf (not tapering at the base) and somewhat longer hairs (up to 1 mm.) than sweet marjoram.

MICROSCOPIC STRUCTURE.—**Petiole** and **Midrib** in cross section are analogous in structure to those of peppermint but are less robustly developed.

Leaf Blade (Fig. 42).—Both *epiderms* between the veinlets have sinuous-walled, sometimes faintly beaded cells with long, broad, jointed, smooth or warty, *pointed hairs*. Over the midrib, veins, and veinlets the cell walls are straight, often strongly beaded, and many of the hairs are narrower and stiffer.

Capitate hairs with short, one- or two-celled stalks and eight- to twelve-celled *bladder glands* occur throughout both epiderms.

The *palisade layer* is one cell thick.

CHIEF STRUCTURAL CHARACTERS.—Leaf spatulate, petioled, downy-hairy on both sides.

Hairs: (1) pointed, long, broad, jointed, smooth or warty, stiff only on petioles, ribs, and veins; (2) capitate with one to two joints. Bladder glands eight- to twelve-celled.

Pot marjoram has hairs up to 1 mm.

CHEMICAL COMPOSITION.—König¹ gives the following analysis of the dry herb:

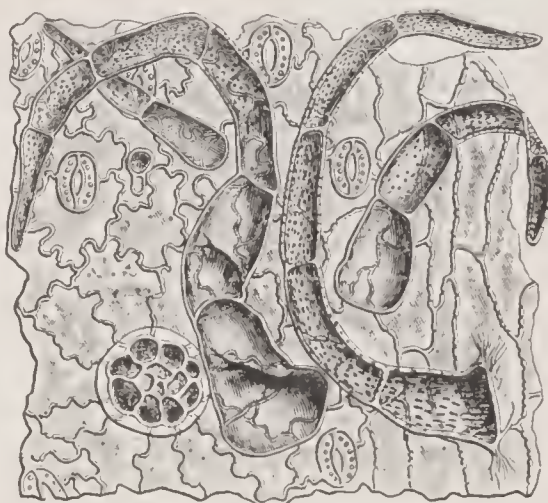


FIG. 42.—Sweet Marjoram. Lower epiderm of leaf in surface view showing straight-walled cells, wavy-walled cells, pointed and capitate hairs, and bladder gland. $\times 160$. (A.L.W.)

Water	Protein	Oil, fixed	Oil, volatile	Pentosans	Fiber	Ash
% 7.61	% 14.31	% 5.60	% 1.72	% 7.68	% 22.06	% 9.69

¹ Chem. mensch. Nahr.-Genussm., Berlin, 1920, 2, 850.

The *U. S. Standards* require that marjoram, consisting of the dried leaves, with or without a small proportion of the flowering tops, contain not more than 16 per cent of total ash, 4.5 per cent of acid-soluble ash, and 10 per cent of stems and harmless foreign matter; also that marjoram extract contain not less than 1 per cent by volume of oil of marjoram.

Volatile Oil.—By Von Fellenberg's chromic acid oxidation method, Zäch ¹ obtained 0.5 to 1 per cent.

Physical and Chemical Values.—The following limits are based on early data, notably as reported by Schimmel & Co.,² also on figures obtained at the Imperial Institute,³ and on Hungarian oils by Janicsek ⁴ and Guenther:⁵

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Ester No.	Acetyl No.*	Acid No.	Sol. 80% alcohol
			°				vols.
Min.	0.890	1.465	+ 5	10	40	0	1
Max.	0.916	1.485	+32	60	80	1.5	2

* Ester number after acetylation.

Constituents.—Less is known as to the constituents of this oil than of most flavoring oils. Blitz ⁶ announced that *terpinene* makes up the greater part of the 40 per cent of total terpenes and that *d-α-terpineol* (C₁₀H₁₈O) is the chief alcohol present. Wallach ⁷ demonstrated that *terpineol-4* is the chief terpeneol, and Reti ⁸ by a new method obtained 65 per cent of *carvacrol*.

Infection of the plant with *Eriophyes thomasi* caused a decrease in the oil of about 11 per cent of thymol, as determined by Salgues.⁹

Pentosans.—In dry matter 8.32 per cent. See also Introduction to Part III.

¹ Mitt. Lebensm. Hyg. 1932, **23**, 156.

² Rep. Oct. 1894, table p. 23; Apr. 1897, table p. 30.

³ Bul. 1913, **11**, 50.

⁴ Mezőgazdasági Kutatások 1929, **2**, 153; Kísérletügyi Közlemények 1934, **37**, 147.

⁵ Am. Perf. 1938, **36**, No. 3, 48.

⁶ Ber. 1899, **32**, 995.

⁷ Ann. 1906, **350**, 169; 1907, **356**, 206; 1907, **357**, 77.

⁸ Ann. chim. appl. 1925, **15**, 317.

⁹ Compt. rend. soc. biol. 1936, **121** 1074.

Mineral Constituents.—Determinations made by Rupp¹ on 36 samples of the air-dry herb grown in Germany and Switzerland showed a range of 6.3 to 24.0 per cent in ash, 0.66 to 14.0 per cent in sand, and 5.4 to 14.3 per cent in sand-free ash. Mehring² gives 10.62 per cent as the average ash content of 156 samples found by 5 analysts.

A small amount of adhering sand is usually present even in the high-grade product, but a limit must be placed that excludes an abnormal amount whether present through accident or design. The limit of 10 per cent total ash allows for a reasonable percentage of sand unavoidably present.

Rupp's analysis of the ash of German and French marjoram follows:

	K ₂ O	Na ₂ O	CaO	MgO	Fe ₂ O ₃	Mn ₃ O ₄	P ₂ O ₅	SO ₃	SiO ₂	Cl	CO ₂
	%	%	%	%	%	%	%	%	%	%	%
German	20.18	0.68	17.60	4.76	7.30	1.05	8.88	4.92	26.52	2.05	6.06
French	18.34	0.65	24.80	6.74	6.06	trace	9.10	4.80	19.44	1.51	8.56

Terpeneless Marjoram Oil.—Klopfer³ gives values as follows: specific gravity at 15° C. 0.937, optical rotation -6° , and phenols 62 per cent.

CHEMICAL COMPOSITION OF OILS OF OTHER SPECIES.—

Analyses by Schimmel & Co.⁴ of Cretian oil from *O. hirtum* Lk. show 60 to 85 per cent of carvacrol and that from *O. Smyrneum* L. 30 to 60 per cent. *Cymol* was present in both and linaloöl in the latter. Pickles,⁵ in Cyprian oil (specific gravity 0.960 to 0.970, optical rotation $+0^{\circ} 10'$ to $+0^{\circ} 30'$) from *O. majoranoides*, found about 84 per cent of carvacrol. In the oil of *O. virens* from plants grown near Messina, Romeo and Giuffré⁶ found: specific gravity at 15° C. 0.9226, refractive index at 25° C. 1.4943, optical rotation at 20° C. $-2^{\circ} 10'$, saponification number 2.10, ester number 1.50, ester number after acetylation 170.7, and soluble in 3 volumes of 75 per cent alcohol. Thymol and carvacrol were present.

¹ Z. angew. Chem. 1892, 5, 681.

² J. Agr. Res. 1924, 29, 569.

³ Schimmel & Co. Rep. 1929, 169.

⁴ Rep. Apr. 1897, table p. 30.

⁵ Trans. Chem. Soc. 1908, 876.

⁶ Ann. chim. appl. 1925, 15, 363.

Oil of *O. Maru* from Cyprus, analyzed at the Imperial Institute,¹ showed: specific gravity at 15° C. 0.904, refractive index at 20° C. 1.4775, optical rotation at 20° C. +9° 27', ester number 4.1, ester number after acetylation 74.5, acid number 4.1, and soluble in 1.4 volumes of 80 per cent alcohol at 15° C.

THYME

Thymus vulgaris L.

Fr. Thym. Sp. Tomillo. It. Timo. Ger. Thymian.

The sweet herb thyme, like savory, has such small leaves as to necessitate gathering the whole blooming tip with stem, leaves, and flowers.

MACROSCOPIC STRUCTURE (Fig. 39, IV).—A fine hoary pubescence characterizes the whole growing tip. Small lavender or pink flowers of the mint type occur in whorls. The leaf is ovate lanceolate, seldom exceeding 12mm.; the petiole is short.

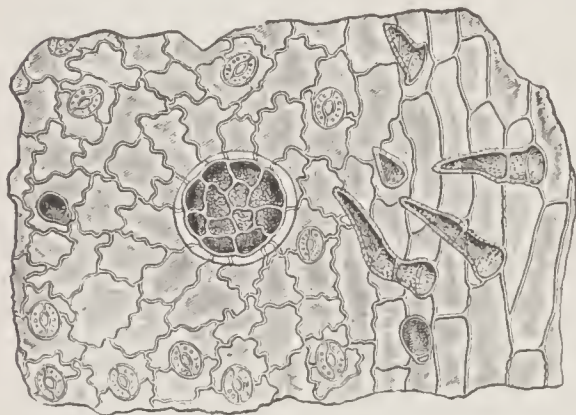


FIG. 43.—Thyme. Lower epiderm of leaf in surface view showing straight-walled cells, wavy-walled cells, pointed and capitate hairs, and bladder gland. $\times 160$. (A.L.W.)

MICROSCOPIC STRUCTURE.

Leaf (Fig. 43).—Compared with those of marjoram and savory the deeply wavy-walled cells and the stomata of both *epiderms* are smaller and the *hairs* are shorter, with narrower bases. Notwithstanding their small size the hairs are stiff and warty.

The *capitate hairs* have small unicellular stalks.

Bladder glands are small, twelve-celled.

CHIEF STRUCTURAL CHARACTERS.—Leaves small, petioled.

Wavy-walled cells, one- to two-celled warty hairs and stomata small; bladder glands twelve-celled.

CHEMICAL COMPOSITION.—So far as the value of this spice as a flavor is concerned, the only constituents that should be considered are those contained in the volatile oil which is present in the air-dry material to the extent of about 1 per cent. The herb, however, should not contain an excess of woody stems or of sand that would render it

¹ Bul. 1925, 23, 421.

objectionable in foods. Such impurities in the ground product would be indicated by high percentages of crude fiber and ash insoluble in acid, but figures are available only on the latter. Mehring gives 9.83 per cent as the average ash content of 104 samples examined by four analysts.

The *U. S. Standards* require that thyme (dried leaves and flowering tops) contain not more than 14 per cent of total ash nor 4 per cent of ash insoluble in hydrochloric acid, and thyme extract not less than 0.2 per cent by volume of thyme oil.

Volatile Oil. *Physical and Chemical Values.*—Formerly Spanish oil was distinguished from French oil by its higher, often more than double, phenol content and consequently higher specific gravity and solubility in 70 and 80 per cent alcohol; furthermore the predominating phenol was carvacrol, whereas in French oil it was thymol. Umney ¹ noted marked differences in the oil of different regions in Spain. More recent examinations of Spanish oil by Parry ² indicate that now, whether owing to difference in variety or improvements in the process or both, thymol is the predominating phenol.

The maximum values, as given in the following table, not only apply to Spanish oils such as Rodie ³ found on the market but are high enough to include the Dalmatian oil examined by Pickles,⁴ the Cyprian oil examined at the Imperial Institute,⁵ and the Calabrian oil examined by La Face,⁶ while the minimum values represent more nearly the South African and Hungarian oils examined by Schimmel & Co.⁷ and Janicsek ⁸ and the Calabrian oil from fresh blossoming twigs reported by La Face.⁹ The results of Umney ¹⁰ are also within the limits.

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Phenols	Sol. 80% alcohol
			°	%	vols.
Min.	0.901	1.4768	−4.0	20	1
Max.	0.955	1.5100	−0.7	70*	2

* Normal French oils, according to Gildemeister and Hoffmann, 30, rarely up to 42%.

¹ Perf. Ess. Oil Rec. 1914, 5, 450.

² Ibid. 1920, 11, 139.

³ Bul. soc. chim. 1907, [4], 1, 236.

⁴ Proc. Chem. Soc. 1911, 27, 285.

⁵ 1924, Bul. 22, 265.

⁶ Parf. France 1926, 4, 366.

⁷ Rep. Oct. 1915, 37.

⁸ Riechstoff Ind. 1928, 3, 211.

⁹ Parf. France 1924, 21, 326.

¹⁰ Perf. Ess. Oil Rec. 1914, 5, 423.

Interesting results on Hungarian oil from the female flowers and hermaphrodite plants respectively, by Janiesek,¹ follow: yield 0.28 and 23 per cent, specific gravity at 15° C. 0.9280 and 0.9206, refractive index at 20° C. 1.5001 and 1.4967, optical rotation 1° 14' and 0° 80', thymol content 52 and 48 per cent.

Constituents.—Mention is made under values of wide variation in the relative amounts of *thymol* and *carvacrol*, as well as in the total phenols representing chiefly the sum of these two. Such variations would be unbelievable were the substances widely dissimilar; however, the fact that both have not only the same empirical formulas but also the same structural formulas, except that the hydroxyl group replaces a different hydrogen of the ring, suggests that some slight difference in physiological activity brings about the change from one to the other. Further investigation may bring out that 20 per cent of total phenols, the minimum of the U. S. Pharmacopœia, should be revised upward.

Thymol was first found by Lallemand, who wrote a series of papers beginning in 1853 and also identified *cymol*.

Labbé,² who considers the presence of pinene as due to adulteration, gives the following average percentage composition: thymol 30, carvacrol trace, *l-linaloöl* 5, *cymol* 21, *borneol* 8, *menthene* 15, and a hydrocarbon (boiling point 155 to 158° C.) 17 per cent. Schimmel & Co.³ state that *l-pinene* is present, although in minute amount; they also report *l-borneol* and its *acetate*, *citral*, *linaloöl*, *geraniol*, *terpineol-4*, *camphor*, *camphene*, and β -*pinene*.

Thymol, methylisopropylphenol, or oxyhydroxycymene, $C_{10}H_{14}O$ or $C_6H_3(CH_3)(OH)(C_3H_7)$, is a well-known and efficient antiseptic much used in mouth washes, etc. The substance may be prepared from oil of thyme or oil of ajowan or may be synthesized from dibromomenthone. The colorless hexagonal crystalline plates melt at 50° and boil at 230° C. They are soluble in alcohol and ether, but only slightly in water.

Carvacrol or isopropyl-*o*-cresol, $C_{10}H_{14}O$ or $C_6H_3(CH_3)(OH)(C_3H_7)$, is an isomer of thymol and occurs with it in oil of thyme. Savory and spearmint oils also contain it. It may be separated from thyme oil, or prepared by synthesis, as a thick, oily, optically inactive substance; specific gravity at 15° 0.981, boiling point 237° C. See also carvone under Peppermint.

¹ Kísérletügyi Közlemények 1934, 37, 147.

² Bul. soc. chim. 1898, [3], 19, 1009; Chem. & Drug. 1899, I, 54, 323.

³ Rep. Oct. 1894, 56; 1922, 65.

Pentosans.—In dry matter 14.74 per cent. See also Introduction to Part III (Hanus and Bien).

CHEMICAL COMPOSITION OF OILS OF OTHER SPECIES.—

T. capitatus H. et K. grown in Sicily yields oil showing specific gravity at 15° C. 0.9582, refractive index at 20° C. 1.5106, optical rotation at 22° C. -0.70° , and phenols (largely carvacrol) up to 80 per cent.¹ Sardinian oil from the same species contained 60 per cent of phenols.²

Oil from Russian-grown *T. odoratissimus* Bieb. showed specific gravity at 15° C. 0.8682, refractive index 1.4755, optical rotation $+15.22^\circ$, and contained only 8 per cent of phenols.³

Wild plants of *T. Serpyllum* L. yielded oil with specific gravity at 15° C. of 0.905 to 0.930, optical rotation of -11 to -10° .⁴ Crimean oil from wild and cultivated *T. Serpyllum* L. gave specific gravity 0.8734 to 0.9448, refractive index 1.4865 to 1.5035, optical rotation -4.4 to $+8.8^\circ$, ester number 15.3 to 31.46, ester number after acetylation 59.4 to 212.⁵

T. striatus Vahl grown in Italy yielded oil showing specific gravity at 15° C. 0.908, refractive index at 24° C. 1.4937, optical rotation at 26° C. -4.3° , esters 2.83 per cent, aldehydes and ketones none.⁶

Spiridonova⁷ obtained from *T. marschallianus* Willd. 0.84 per cent of volatile oil of a light color and an agreeable odor differing from that of common thyme oil. It showed specific gravity 20°/20° 0.9025 and refractive index at 20° C. 1.493, and contained α -pinene 10.7, camphene 3.6, sabinene 9.9, *p*-cymene 8.1, undecylic acid 0.2, ammonium hydroxide 2, carvacrol 3.1, thymol 5.5, borneol about 30, sesquiterpenes 16.8 (containing some cadinene), and resins 1.8 per cent.

¹ Palazzo and Lutri: Ann. chim. appl. 1924, **14**, 103.

² Puxeddu: Ibid. 1926, **16**, 323.

³ Chernukhin: Trans. Sci. Chem. Pharm. Inst. Moscow 1928, **19**, 196; in English p. 201.

⁴ Schimmel & Co.: Rep. Apr. 1897, table p. 48.

⁵ Rutovskii et al.: ibid. 1925, **11**, 59.

⁶ Leone and Angelescu: Gaz. chim. ital. 1922, **52**, I, 152.

⁷ J. Gen. Chem. (U.S.S.R.) 1936, **6**, 1510.

SUMMER SAVORY

Satureia hortensis L.

Fr. Sarriette. Sp. Ajedrea. It. Santoreggia. Ger. Bohnenkraut.

Leaves and flowering tips of two species of the genus *Satureia*, both natives of the Mediterranean region, are used as spices. Of these summer savory, an annual plant, in addition to being a garden herb furnishes the savory of commerce, while winter savory (*S. montana* L.) is especially valuable in the garden because it is a perennial.

MACROSCOPIC STRUCTURE.—The plant is pubescent throughout, the longest hairs occurring on the margins of the lower half of the leaf. The leaf (Fig. 39, III) is entire, narrow, pointed at the tip,

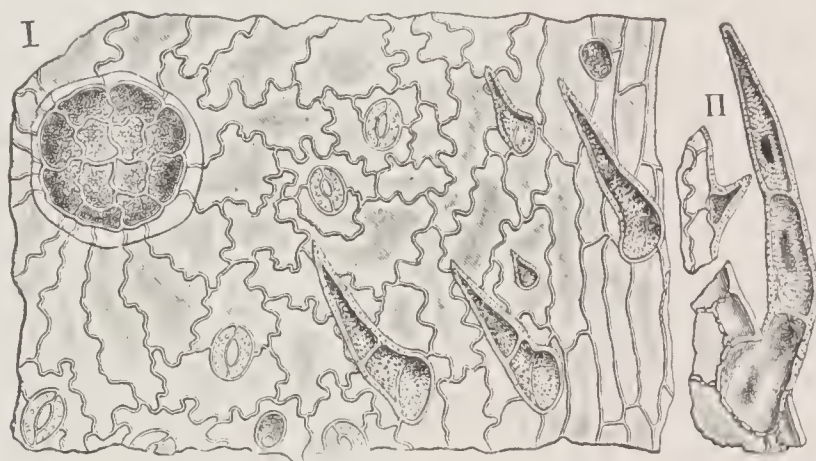


FIG. 44.—Savory. Lower epiderm of leaf in surface view. I straight-walled cells, sinuous-walled cells, pointed and capitate hairs, and bladder gland. II hairs from margin near base. $\times 160$. (A.L.W.)

and tapering at the base to the scarcely evident petiole. Under a lens the leaves appear finely pitted owing to the depressions beneath the bladder glands. Numerous lavender flowers, up to 5 mm. broad and 5 mm. long, on short pedicels, occur in groups of three in the axils of the leaves. The deeply five-cleft calyx is half the length of the whole flower.

MICROSCOPIC STRUCTURE (Fig. 44).—Stiff, warty, pointed hairs occur on leaves, calyx, and stem; on the edge of the leaf, near the base, they reach nearly 1 mm. in length and have as many as five joints.

Capitate hairs on short, unicellular stalks and exceptionally large bladder glands with twelve cells occur on both leaf surfaces.

CHIEF STRUCTURAL CHARACTERS.—Leaves entire, narrow tapering, nearly sessile. Flowers small.

Leaves, calyx, and stem with jointed, warty, pointed hairs, longest at margins of leaf near base; capitate hairs nearly sessile; bladder glands twelve-celled, large.

CHEMICAL COMPOSITION.—An analysis by Dahlen,¹ of the green herb (leaves and flowering tops) collected at the end of the blooming period, follows:

Water	Protein	Fat	N-f. ext.	Sugar	Fiber	Ash
%	%	%	%	%	%	%
71.88	4.15	1.65	11.16	2.45	8.60	2.11

The *U. S. Standards* require that savory extract contain 0.35 per cent by volume of savory oil.

Volatile Oil.—The dried herb contains up to about 1 per cent of volatile oil.

Physical and Chemical Values.—Schimmel & Co. in an early report² give specific gravity at 15° C. 0.904 and 0.913 and optical rotation +0° 4', but in a later report give yield 0.09 per cent, specific gravity at 20° C. 0.958, phenols 38 per cent, and soluble in 10 volumes of 80 per cent alcohol. Albricci³ gives specific gravity at 15° C. 0.896, optical rotation 0°, saponification number 5.6, and phenols 31 per cent. Gildemeister and Hoffmann in the last German edition give specific gravity at 15° C. 0.896 to 0.960, optical rotation −0° 56' to +0° 4', phenols 30 to 42 per cent, and soluble in 2 volumes of 80 per cent alcohol.

Fayaud⁴ has shown that the oil from leaves gathered when in bloom is yellow and has a specific gravity at 15° C. of 0.870 and polarizes −0.62° at 15° C. When the herb is gathered in June before lignification sets in the oil is green and has the following values: specific gravity at 15° C. 0.8959, refractive index 1.4742, optical rotation +5.20°, total phenols 12 per cent, and soluble in 1.1 volumes of 90 per cent alcohol.

Constituents.—*Carvacrol* (see *Thyme*), first found by Jahns,⁵ of which 30 per cent or more is present, appears to be the chief odorous constituent. The same author obtained evidence of another phenol.

¹ Landw. Jahrb. 1874, 3, 312.

² Rep. Oct. 1897, 59.

³ Rev. ital. ess. prof. 1925, 7, 16.

⁴ Riv. ital. ess. prof.; Parf. mod. 1926, 19, 75.

⁵ Ber. 1882, 15, 816.

The terpenes present are probably *cymene*, *pinene*, and *dipentene*. Gildemeister and Hoffmann¹ mention *cymol* and a terpene.

Pentosans.—In dry matter 11.95 per cent. See also Introduction to Part III (Hanus and Bien).

Mineral Constituents.—Mehring² gives 9.94 per cent of ash as the average of 29 samples by four analysts of air-dry herb, believed to be pure.

CHEMICAL COMPOSITION OF OILS OF OTHER SPECIES.—*S. Thymbra* L., grown in Spain, contains according to Blaque³ 19 per cent of thymol.

Winter Savory (*S. montana* L.).—Schimmel & Co.⁴ give the following results: yield 0.18 per cent, specific gravity 0.939, optical rotation $-2^{\circ} 35'$, and soluble in 1.5 volumes of 80 per cent alcohol, also phenols 65 per cent. Paulet⁵ reports: yield 0.1 to 0.2 per cent of oil showing specific gravity at 15° C. 0.924, refractive index at 20° C. 1.4918, optical rotation $+2.8^{\circ}$, ester number 7.5, and soluble in 2.1 volumes of 80 per cent alcohol. In addition to terpenes, 32 per cent of carvacrol is present.

S. nepeta (L) Scheele, according to Pellini,⁶ yields 0.47 per cent of oil when fresh and up to 1 per cent when dry. The oil contains about 66 per cent of ketones including pulegone.

S. Calamintha, dried, yields according to Nylov and Williams⁷ about 1 per cent of oil with specific gravity of 0.977, refractive index 1.4829, optical rotation $+13.3^{\circ}$, ester number 63.6, and acid number 21.12.

ROSEMARY

Rosmarinus officinalis L.

Fr. Romarin. Sp. Romero. It. Rosmarino. Ger. Rosmarin.

A plant with such tender associations and so euphonious a name seems worthy of more attention than it receives in the prosaic New World. It is a small shrub, a native of the Mediterranean region.

¹ Ätherische Öle, Leipzig, 3 Aufl. 1931, **3**, 722.

² J. Agr. Res. 1924, **29**, 569.

³ Bul. sci. pharmacol. 1923, **30**, 201.

⁴ Rep. Oct. 1897, 59.

⁵ Parf. mod. 1926, **19**, 311.

⁶ Ann. chim. appl. 1923, **13**, 97.

⁷ Parf. mod. 1929, **22**, 577.

MACROSCOPIC STRUCTURE.—The *leaves* are narrow, linear, revolute on the margins, hoary beneath. The *flowers* are light blue, axillary.

MICROSCOPIC STRUCTURE.—The cells of the *upper epiderm* are larger and more often beaded than those of the *lower epiderm*. Hairs are not numerous.

The *lower epiderm* (Fig. 45), in addition to sinuous-walled cells and eight-celled *bladder glands* analogous to other members of the family, is characterized by long thin-walled, non-warty, *branching hairs* and jointed *capitate hairs*.

The *branching hairs* are most striking on the veins and veinlets. *Capitate hairs* arise not only from among the epidermal cells but also from joints of the hairs; that is, the ends of hair branches, which normally are pointed, may bear a globular head.

Flückiger¹ notes the presence of a collenchymatous *hypoderm* forming a single row, under the upper epiderm or wedge-shaped groups at the veins; this, however, does not form a continuous layer and is not a well-marked distinction.

Palisade cells form one to three layers.

CHIEF STRUCTURAL CHARACTERS.—Leaves narrow, hoary beneath.

Hairs thin-walled, branching, sometimes with globular heads on the branches, also jointed capitate. Bladder glands eight-celled.

CHEMICAL COMPOSITION. Volatile Oil.—The amount available varies within the general range of the family up to 2 per cent or over.

The *Physical and Chemical Values* given below are in accordance with early results and more recent quite divergent results on French,

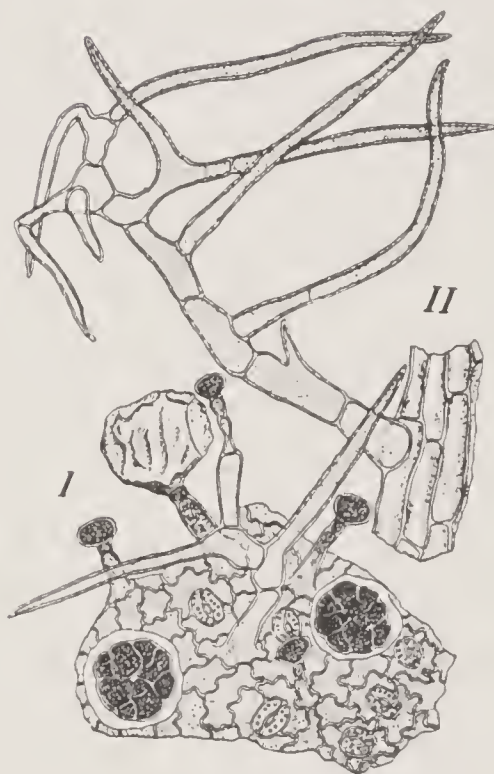


FIG. 45.—Rosemary. Lower epiderm of leaf in surface view. *I* between veins showing sinuous-walled cells, branching and capitate hairs, and bladder glands. *II* over vein showing elongated cells and branching hair. $\times 160$. (A.L.W.)

¹ Pharmakognosie, Berlin, 1891, p. 739.

English, Spanish, and Greek oils by Schimmel & Co.,¹ on Italian oils by Traetta-Mosca and Papocchia,² on French and Dalmatian oils by Massera,³ on Sicilian oils by Pellini and Morani,⁴ on Spanish and French oils by Parry,⁵ on Crimean and Ssuchum oils by Rutovskii et al.,⁶ and on Moroccan oil by Guenther.⁷ Formerly it was believed that genuine oil polarized only to the right, but Henderson⁸ and others have abundantly shown that oils polarizing to the left are not unusual. Massera gives -40° as the minimum for French oils. Excepting this, the minimum of available results is -13° . The acid number of Ssuchum oil reaches 7.8 and is not included.

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Ester No.	Acetyl No.*	Acid No.	Esters †	Alcohols, total‡	Alcohols, free‡	Sol. 80% alcohol
			°				%	%	%	vols.
Min...	0.891	1.4650	-40	6.5§	28	0.4	2.3	9	6.1	1.0
Max..	0.933	1.4735	+15	20.0	60	2.0	6.1	20	10.4	6.6

* Ester number after acetylation. † As bornyl acetate. ‡ As borneol. § Rarely 2. || Russian 78.

Constituents.—*Borneol* and α -*pinene* were reported by Bruylants;⁹ the latter, also *camphene*, by Gildemeister and Stephan;¹⁰ *cineol* by Weber;¹¹ *camphor* by Lallemand;¹² a sesquiterpene, probably *caryophyllene*, by Haller;¹³ and *bornyl acetate* by several chemists. Rutovskii and Vinogradova¹⁴ regard *camphylene* as a probable constituent of Russian oil. Traetta-Mosca and Papocchia,¹⁵ in different fractions of oil from fresh rosemary flowers, found amounts of cineol totaling 25.98 per cent, also borneol (partly as acetate), pinene, camphor, and what appeared to be camphene.

¹ Rep. Apr. 1910, 93; Oct. 1910, 111.

² Ann. chim. appl. 1923, 13, 326.

³ Riv. ital. ess. prof. 1923, 5, 7.

⁴ Ibid. 1923, 5, 113.

⁵ Parf. mod. 1924, 17, 232.

⁶ Arb. Chem. Pharm. Inst. Moskaus, 1925, 11, 59, 93.

⁷ Drug Cosm. Ind. 1938, 42, 439.

⁸ Pharm. J. 1907, 79, 599.

⁹ J. pharm. chim. 1879, [3], 29, 508.

¹⁰ Arch. Pharm. 1897, 235, 586.

¹¹ Ann. 1887, 238, 89.

¹² Ibid. 1860, 114, 197.

¹³ Compt. rend. 1889, 108, 1308.

¹⁴ Trav. inst. pharm. Moscou 1927, 17, 86.

¹⁵ Loc. cit.

SAGE

Salvia officinalis L.

Fr. Suage. Sp. Salvia. It. Salvia. Ger. Salbei.

In the United States, at least, sage, the leaf and petiole of a small woody plant, is the most popular leaf spice. It is grown to some extent in the kitchen garden and on a commercial scale, but the dry leaf is largely imported from Italy and other parts of Europe. Although a perennial and grown as such in the garden, it is customary in field culture to seed each year or else plant cuttings or layers from mother plants.

Sage is best known in conjunction with black or white pepper as the seasoning for pork sausage and, together with other spices, as an ingredient of poultry seasoning. It is also the characteristic ingredient of sage cheese, the chopped leaves imparting a pleasing color as well as flavor.

There are a number of varieties differing in the color of the leaves (green, yellow, reddish, spotted, and variegated) and to some extent in the size and shape of the leaves.

MACROSCOPIC STRUCTURE.—Marked variations in the shape of the leaves (Fig. 39, I) are noticeable even when produced by the same plant. Some are lobed at the base, others entire. The end may be pointed or blunt. The leaf blade ranges up to 7 cm. long and the petiole up to 4 cm.

Characteristic of the leaves are the warty upper surface, due to the depression of the veinlets, and numerous long hairs forming a whitish down on the petioles and both surfaces of the young leaves, disappearing to a large extent during later growth.

MICROSCOPIC STRUCTURE.—**Petiole** and **Midrib** conform to the family type as described in the general section, the *collenchyma* being well developed.

Leaf Blade.—*Lower* and *upper epiderms* are practically the same except that in the former the walls of the cells between the veinlets are somewhat more sinuous. *Hesperidin* crystals are often present.

Characteristic are the long, slender, sinuous, jointed, non-warty *pointed hairs* (Fig. 46, I). Shorter unicellular forms also occur and, over the midrib and large veins, thicker-walled, *warty hairs* (II).

Capitate hairs, with unicellular or dicellular head, some nearly sessile (hydrothodes of Mitlacher), others with one- or more celled stalk (resin glands of Mitlacher), are numerous.

Bladder glands of the type with twelve-celled head (Fig. 46, I, above center) occur in considerable numbers. Eight-celled glands may be present but never with eight partition walls extending symmetrically to the very center as shown by some authors.

Palisade cells form one to three rows.

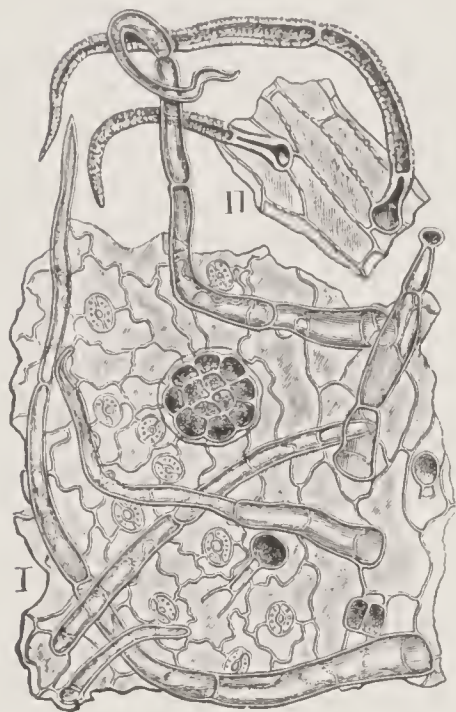


FIG. 46.—Sage. Lower epiderm of leaf in surface view. I straight-walled and wavy-walled cells, pointed and capitate hairs, and bladder gland. II cells and hairs over large vein. $\times 160$. (A.L.W.)

CHIEF STRUCTURAL CHARACTERS. — Leaf pointed or blunt, up to 7cm., “warty” on upper surface, with felt of long hairs on both surfaces when young.

Pointed hairs mostly narrow, long, jointed, thin-walled, non-warty; capitate forms with one- to several-celled stalk. Bladder glands commonly twelve-celled.

CHEMICAL COMPOSITION. — The average of 311 determinations by two analysts, as given by Mehring,¹ shows 7.39 per cent of ash.

The *U. S. Standards* require that sage (leaves only) contain not less than 1 per cent of volatile ether extract and not more than 25 per cent of fiber, 10 per cent of total ash, nor 1 per cent of sand.

Volatile Oil.—The content of volatile oil ranges up to 2.5 per cent calculated to the air-dry material. Viehoever and Clevenger² found that in the leaves the percentage is about three times that in the stems.

Physical and Chemical Values.—Schimmel and Co.³ and Umney and Bennet⁴ have published comprehensive articles giving values. Harvey⁵ gives limits for Dalmatian oil, an anonymous author⁶ for Spanish oil, Simmons⁷ for the product of the post-war period, and Fölsch⁸ and Janicsek⁹ for Hungarian oil. Parry¹⁰ and Gildemeister

¹ J. Agr. Res. 1924, 29, 569.

² J. Am. Pharm. Ass. 1920, 9, 563.

³ Rep. Oct. 1894, 51; Oct. 1895, 40; 1911, 79; 1929, 82.

⁴ Pharm. J. 1906.

⁵ Chem. Drug. 1908, 69 No. 1493, 393.

⁶ Perf. Ess. Oil Rec. 1914, 5, 22.

⁷ Ibid. 1925, 16, 80.

⁸ Riechstoff Ind. 1928, 3, 181.

⁹ Ibid. p. 211.

¹⁰ Chem. Essen. Oils Artif. Perfumes, London. 3rd Ed. 1918.

and Hoffmann¹ give separate limits for Dalmatian or German and for Spanish oils. The following limits cover both types:

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Ester No.	Acetyl No.*	Alcohols as borneol	Sol. 80% alcohol
			°			%	vols.
Min. . .	0.913	1.4575	+ 1	5	30	9	1
Max. . .	0.936	1.4690	+26	36	95	29	2

* Ester number after acetylation.

Values for oil from sage grown in Corfu and Cyprus, as published by Schimmel & Co.,² fall within the above limits except that the optical rotation is -15.2 to -6.5° .

Constituents.—*Borneol* (see p. 185) is one of the chief constituents, but the ketone *thujone* is the constituent imparting the characteristic flavor. *Thujone* (under the name of *salviol*) was isolated from sage and studied by Muir and by Muir and Sugiura.³ Wallach⁴ found *cineol* and the terpene *d- α -pinene*. Schimmel & Co.⁵ found that *d-camphor* sometimes is present. *Salvene* ($C_{10}H_{18}$) was found by Seyler⁶ in Dalmatian oil. In Spanish sage Dorronsora⁷ identified *cineol* (large amount), *linaloöl*, *linalyl acetate* and *isovalerianate*, *d-camphor*, *camphene* (probably), *pinene* (?), and *dipentene* (?).

Thujone, $C_{10}H_{16}O$ or $C_6H_6(C_3H_7)(CO)(CH_3)$, is a colorless, odorous liquid with a specific gravity at $20^\circ C.$ of 0.916 and a boiling point of about $203^\circ C.$; *d- β* and *l- α* modifications were identified by Wallach⁸ in sage. Under the name of *tanacetone* it was isolated from oil of tansy, and under the name of *thujone* from oil of cedar (*Thuja*).

Morani⁹ gives analyses of levorotatory Italian oil from flower

¹ Ätherischen Öle, Leipzig, 3 Aufl. 1931, **3**, 691.

² Rep. Apr. 1909, 82; 1910, 112.

³ Phil. Mag. 1877, **4**, 336; also other papers in English journals 1877 to 1880.

⁴ Ann. 1885, **227**, 277; 1895, **286**, 93.

⁵ Rep. Oct. 1907, 83.

⁶ Ber. 1902, **35**, 550.

⁷ Mem. real. acad. cienc. Madrid 1919, **29**.

⁸ Ann. 1904, **336**, 270.

⁹ Nuovi ann. agr. 1928, **7**, 25.

heads or whole plants gathered in Spring and Summer and from the whole plant when not in bloom in Winter:

	Esters	Cineol	Borneol	Camphor and thujone	Sesqui- terpenes	Terpenes
	%	%	%	%	%	%
Spring and Summer. .	2	32-35	9-14	5-10	20
Winter.....	2.2-3.7	13-20	7.5-12	20-32	30	15

Pentosans.—In dry matter 9.59 per cent. See also Introduction to Part III (Hanus and Bien).

CLARY

Salvia Sclarea L. = *S. bracteata* Sims.

Fr. Sauge sclarée. Ger. Muskateller Salbei.

Clary, clary sage, or muscatel sage is grown as a pot herb and for oil production, but appears to be of limited importance. It is a native of southern Europe and like true sage is a perennial, but is commonly grown as a biennial. Several varieties, varying in height and color of flower and bracts, are grown throughout southern Europe and the Orient.

Clary Oil.—*Physical and Chemical Values* on 2 samples of known purity, given by Chiris,¹ and the range for numerous oils of southern France by Igolen,² follow:

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Ester No.	Formyl No.*	Acid No.	Esters†	Alcohols, total‡	Alcohols, free‡	Alcohols, com- bined‡
Chiris:			°				%	%	%	%
I	0.964	−13.0	152.0	255.5	0.42	53.27	74.42	32.56	41.86
II	0.897	−17.9	110.6	236.3	0.42	38.71	69.60	39.18	30.42
Igolen:										
Min.	0.897	1.4648	−7	140.0	238.9	0.1	49.0			
Max.	0.911	1.4658	−20	194.1	259.7	0.7	67.9			

* Ester number after formylation. † As linalyl acetate. ‡ As linaloöl.

¹ Parf. France 1924, 19, 263.

² Ibid. 1934, 12, 34.

French oil, according to Roure-Bertrand fils,¹ shows: specific gravity at 15° C. 0.896 to 0.930 and optical rotation -11 to -63° ; also, according to Gildemeister and Hoffmann,² refractive index at 20° C. 1.466 to 1.476 and ester number 110 to 206.

Gildemeister and Hoffmann give the following values for German oil: specific gravity at 15° C. 0.910 to 0.970, refractive index at 20° C. 1.468 to 1.510, optical rotation -66 to $+1.8^\circ$, ester number 18 to 188, and acid number 1 to 17.

In two Hungarian oils³ were found: specific gravity at 15° C. 0.9043, refractive index at 20° C. 1.4648, optical rotation -24° , ester number 158.86, esters 70 per cent, esterified linaloöl 43.68 per cent, and free linaloöl 6.74 per cent. Guenther⁴ gives the following range for Hungarian oils: specific gravity at 15° C. 0.9072 to 0.9328, optical rotation 13.5 to 28.3° , linalyl acetate 60 to 63 per cent, usually soluble in 1 volume of 90 per cent alcohol with marked opalescence and separation of crystals with more alcohol.

Albricci⁵ in Calabrian oil found lower rotation (-30.8°) and much less free alcohols (4.34 per cent) and esters (37.20 per cent) than given by Chiris, but specific gravity at 15° C. (0.8990) was intermediate.

Oil from wild clary, examined by Mollard,⁶ polarized -69.8° , and oil from stems of cultivated plants contained only 15.92 per cent of esters.

Constituents.—Roure-Bertrand fils⁷ showed that *l*-linaloöl is the chief constituent. Schimmel & Co.⁸ had previously isolated *linalyl acetate*.

Kopp⁹ notes that Roumanian oil showed 41.8 to 59.2 per cent of linalyl acetate and 13.8 to 26.5 per cent of linaloöl.

Results by Chiris¹⁰ indicate that esters are formed from free alcohol in the plant.

Sclareol, $C_{20}H_{36}O_2$, obtained from clary as colorless prisms or

¹ Rep. Apr. 1906, 40; Parf. mod. 1912, 5, 93.

² Ätherischen Öle, Leipzig, 3 Aufl. 1931, 3, 701.

³ Mezőgazdasági Kutatások 1929, 2, 153; Kísérletügyi Közlemények 1934, 37, 147.

⁴ Am. Perf. 1938, 36, No. 3, 48.

⁵ Riv. ital. ess. prof. 1926, 8, 21.

⁶ Parf. France 1924, 19, 253.

⁷ Rep. Apr. 1908, 10.

⁸ Rep. Apr. 1897, Table p. 42.

⁹ Pharm. Zentralh. 1928, 69, 677.

¹⁰ Loc. cit.; Parf. France 1924, 20, 292.

needles melting at 105.5 to 106° C. (corrected) by Janot,¹ is believed to contain 2 cycles of the naphthalenic type, 2 tertiary hydroxyls, and a terminal double bond.

Guseva and Guseva² identified *l*-linalool, *l*-linalyl acetate, *l*-nerolidol and its acetate, a sesquiterpene similar to β -santalene; Glichitch and Naves,³ however, consider some of their evidence inconclusive.

¹ Comp. rend. 1930, **191**, 847; 1931, **192**, 845; Ann. Chim., 1932, **17**, 5.

² Riechstoff Ind. 1932, **7**, 65, 78.

³ Parf. France 1932, **10**, 210.

STEMS AND LEAVES OF THE COMPOSITE FAMILY

(*Compositæ*)

MANY species of this family have strong smelling or bitter tasting leaves and flowers, but comparatively few have flavors acceptable in foods. Tarragon is an exception.

TARRAGON

Artemisia Dracunculus L.

Fr. Estragon. Sp. Tarragona. It. Targone. Ger. Estragon.

The original habitat of tarragon is western Siberia southward. It is much cultivated in Persia and other parts of western Asia, also in Europe, especially France, where tarragon oil is prepared by distillation and tarragon vinegar by maceration. It is also a valuable flavoring for salads, sauces, pickles, and various condiments.

Although a member of the same genus as wormwood, a proverbially bitter plant, it has a delightful, aniselike fragrance.

MACROSCOPIC STRUCTURE.—The leaves are linear-pointed, sessile, reaching 8 cm. in length but hardly 1 cm. in width. The midrib and two ribs, one each side, running along the margin from base to tip, are conspicuous, even in young leaves in which the veins are indistinct.

MICROSCOPIC STRUCTURE. Stem.—While still young and tender six zones are well developed. (1) *epiderm* of thin-walled, indistinctly beaded, somewhat elongated cells and stomata; (2) *collenchyma* a few cells thick, except in the ribs where it is more strongly developed; (3) *cortex* of rounded cells containing chlorophyll with a ring of oleoresin ducts in the inner part; (4) *bast fibers* in groups alternating with the oleoresin ducts; (5) *fibro-vascular bundle ring*; and (6) *pith* of finely porous parenchyma.



FIG. 47.—Tarragon. Lower epiderm of leaf in surface view showing stoma, hair scar, and *t* capitate hair. $\times 160$. (K.B.W.)

Leaf (Fig. 47).—Both *epiderms* are much alike, the cells over the veins being elongated, straight-walled, faintly beaded, and striated, while between the veins they are sinuous-walled, especially on the lower epiderm. Stomata and short capitate hairs, with short one- or more celled stalk and two-celled head, occur here and there.

Palisade cells occur on both sides of the leaf, being usually in two rows on the upper side and one row on the lower. The remainder of the *mesophyl* forms a thin layer through which run the *fibro-vascular bundles*. Accompanying each bundle of the midrib, on the upper side, is a large *oleoresin duct* like those of the stem.

CHIEF STRUCTURAL CHARACTERS.—Leaf narrow, sessile, smooth.

Epiderms characterless except for short capitate hairs with two-celled heads; palisade cells on both sides of leaf; oleoresin ducts form ring in inner cortex, and a large one occurs on upper side of midrib of leaf.

CHEMICAL COMPOSITION.—Dahlen’s analysis¹ of the potherb follows:

Water	Protein	Fat	N-f. ext.	Fiber	Ash	P ₂ O ₅	Org. S
%	%	%	%	%	%	%	%
79.01	5.56	1.16	9.46	2.26	2.55	0.24	0.08

Volatile Oil. Physical and Chemical Values.—The physical values for tarragon oil below are those reported by Floriane² amplified by results of earlier authors; the chemical values are credited to Gilde-meister and Hoffmann.³ The values for the terpeneless (terpene- and sesquiterpene-free) oil are by Klopfer.⁴

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Ester No.	Acetyl No.*	Acid No.	Sol. 80% alcohol
			°				vols.
Volatile oil:							
Min.	0.900	1.5028	+2	1	15	0	6
Max.	0.981	1.5160	+9	9	22	1	11
Terpeneless....	0.975	1.5206	+	3

* Ester number after acetylation.

¹ Landw. Jahrb. 1874, 3, 312; 1875, 4, 613.
² Parf. mod. 1922, 15, 229.
³ Ätherischen Öle, Leipzig, 3 Aufl. 1931, 3, 1000.
⁴ Schimmel & Co. Ber. 1929, 169.

In comparison with the foregoing figures, Kazakewicz and Sobolewskaja¹ obtained a lower refractive index (1.4712 to 1.490) and a higher rotation (+20 to +30), also ester number 7.4 to 13.9 and ester number after acetylation 30 to 42.

Constituents.—*Methyl chavicol* (see Anise), shown by Schimmel & Co.² to be identical with the estragol of Grimaux,³ is the chief constituent. Floriane⁴ gives *phellandrene* and *ocimene* (see Basil) as additional constituents.

¹ J. Exp. Agr. Southeastern Russia, 1928, **5**, 157.

² Rep. Apr. 1892, 30.

³ Compt. rend. 1893, **117**, 1089.

⁴ Loc. cit.

BARK SPICES

CIVILIZED man does not resort to barks for nutriment, unless to avert starvation, but he does employ certain barks or the volatile oils from them to impart agreeable flavors to true foods.

All the barks of the spice trade are products of trees of the laurel family. A few others, such as the bark of *Canella alba* Muss. (*Canelaceæ*), although used locally as spices are better classed with drugs.

Birch bark and sassafras (root) bark are not spices but long have been used in making root beer. On distillation they yield volatile oils valuable for flavoring confectionery and beverages.

Barks separate from the trunk through the cambium layer and therefore consist of cork, together with epiderm if not sloughed off, cortex including pericycle, and bast or phloem. By scraping, the outer layers up to the pericycle may be wholly or partially removed. Vessels and other xylem elements are lacking except such as may occur in bundles that penetrate through the bark to leaves and branches.

BARKS OF THE BIRCH FAMILY

(*Betulaceæ*)

THE species described below yields a volatile oil practically identical with that of wintergreen berries.

BIRCH

Betula lenta L.

Fr. Bouleau. It. Betula. Ger. Birke.

The bark of the sweet or black birch, as every country boy in the northeastern section of the United States well knows, has an agreeable aromatic flavor quite like that of wintergreen. The bark itself does not enter commerce, but the twigs are distilled near the place of growth for the manufacture of the volatile oil.

Oil of Sweet Birch or oil of betula and synthetic methyl salicylate have almost entirely replaced oil made from the wintergreen plant (*Gaultheria*) both as a drug and a flavor.

Physical and Chemical Values.—The *U. S. Standards* ignore oil of birch. They specify that wintergreen extract contain 3 per cent by volume of true wintergreen oil. The specific gravity at 25° C. of oil of sweet birch is given as 1.176 to 1.182, of synthetic methyl salicylate as 1.180 to 1.185. Oil of wintergreen is not distinguishable from oil of birch by its specific gravity but is slightly levorotatory (up to -1.5°), whereas oil of birch is inactive. Both oils and methyl salicylate are stated to boil between 219 and 221° C.

Chiris,¹ who describes tests for birch and wintergreen oils and methyl salicylate, gives the following values for an oil of known purity: specific gravity at 15° C. 1.1864, refractive index at 20° C. 1.5368, ester number 359.8, acid number 2.8, esters as methyl salicylate 97.7 per cent, and soluble in 8 volumes of 70 per cent alcohol at 20° C.

Constituents.—Power and Kleber² showed that oil of birch contains 99.8 per cent of *methyl salicylate* and that oil of wintergreen contains slightly less, owing to the presence of a *secondary alcohol* ($C_8H_{16}O$), its aldehyde (*oenanthaldehyde* ?), and its ester with the acid $C_6H_{10}O_2$, also a paraffin *tricontane* ($C_{30}H_{62}$?). Whether or not because of one of these minor constituents, Chiris found that, if 5 drops of wintergreen oil are shaken with 5 drops of 5 per cent alcoholic vanillin and 1 cc. of alcohol, and the mixture then shaken with 2 cc. of concentrated sulphuric acid, a deep red color appears. Birch oil gives a lighter color, deepening on standing; synthetic methyl salicylate gives a yellow color.

CHEMICAL COMPOSITION OF OILS OF OTHER SPECIES.—

Gaultheria punctata Blume. Two samples of oil analyzed by Schimmel & Co.³ showed: specific gravity at 15° C. 1.1861 and 1.1873, refractive index at 20° C. 1.5364, optical rotation 0°, ester number 364.9 and 356.6, acid number 5.4 and 4.8, equivalent methyl salicylate 99.0 and 96.8 per cent; they were soluble in 7 and 8 volumes of 70 per cent alcohol.

G. fragrantissima Wall, grown in Assam, yielded plants containing, according to Singh,⁴ 0.65 per cent of oil which showed: specific gravity at 16° C. 1.185, refractive index at 25° C. 1.4000 (?), optical rotation 0°, saponification number 362.9, equivalent methyl salicylate 99.14 per cent; it was soluble in 6 parts of 70 per cent alcohol.

¹ Parf. France 1924, 17, 192.

² Pharm. Rundsch. 1895, 13, 228.

³ Rep. 1922, 79.

⁴ Indian Forest Rec. 1917, 5, VIII, 33.

BARKS OF THE LAUREL FAMILY

(*Lauraceæ*)

SASSAFRAS belongs to this family, but only the volatile oil enters into foods. Camphor, useful as a drug, is the product of another tree of the family. Clove bark from *Dicypellium caryophyllatum* Nees, a native of Brazil, is marketed in compound quills like Ceylon cinnamon. Although said to serve as a spice, it is known with us only as a drug.

CASSIA AND CINNAMON.—The import trade recognizes two barks, namely cassia and cinnamon or Ceylon cinnamon. Three types of cassia (China, Batavia, and Saigon), named from alleged ports of shipment, are commonly imported into the United States. Each has more or less distinct physical and microscopic characters.

COMPARATIVE MICROSCOPIC STRUCTURE.—The following statements of salient histological characters are offered as a guide, not as an infallible means of distinction.

China Cassia. Pericycle stone cells little thickened on outer side; bast fibers few; starch grains large; oleoresin and mucilage cells not numerous; medullary crystals narrow.

Batavia Cassia. Starch grains small; mucilage cells numerous; medullary crystals broad. Otherwise like China cassia.

Saigon Cassia. Thin bark like China cassia except that oleoresin cells are larger and more numerous. Thick bark with large phloem groups of elongated stone cells, broad medullary crystals, and large oleoresin cells.

Ceylon Cinnamon. Pericycle stone cells more uniformly thickened, bast fibers more numerous, and starch grains smaller than in China cassia; medullary crystals broad.

COMPARATIVE CHEMICAL COMPOSITION.—*Starch* and *fiber* each form about 25 per cent of the cassias, whereas starch is present in lesser and fiber in greater amount in cinnamon, the ratio on the average being approximately 1 : 2. Batavia cassia contains a *mucilaginous substance* forming a gel with water or dilute alcohol.

The *volatile oil* in Saigon cassia ranges up to 5 per cent or over but in the other varieties of cassia and in cinnamon seldom exceeds half that amount. Cinnamal forms about 75 per cent of the volatile

oil of both cassia and cinnamon, but the latter is characterized by the presence of eugenol.

CHINA CASSIA

Cinnamomum Cassia Bl. = *C. aromaticum* Nees

Fr. Cannelle de Chine. Sp. Canela. It. Canella di Ceylan.

Ger. Zimtkassie.

The bark, known in commerce as China cassia, comes into the market largely from China but is also produced throughout south-eastern Asia and the East Indies. The tree has been introduced into tropical and subtropical America. Of the different grades, the best is not equal in pungency to Batavia cassia and vastly inferior to Saigon cassia. Though the thickness of the bark and care with which it is scraped influence in some degree the strength and flavor, the chief factor is inherent in the species.

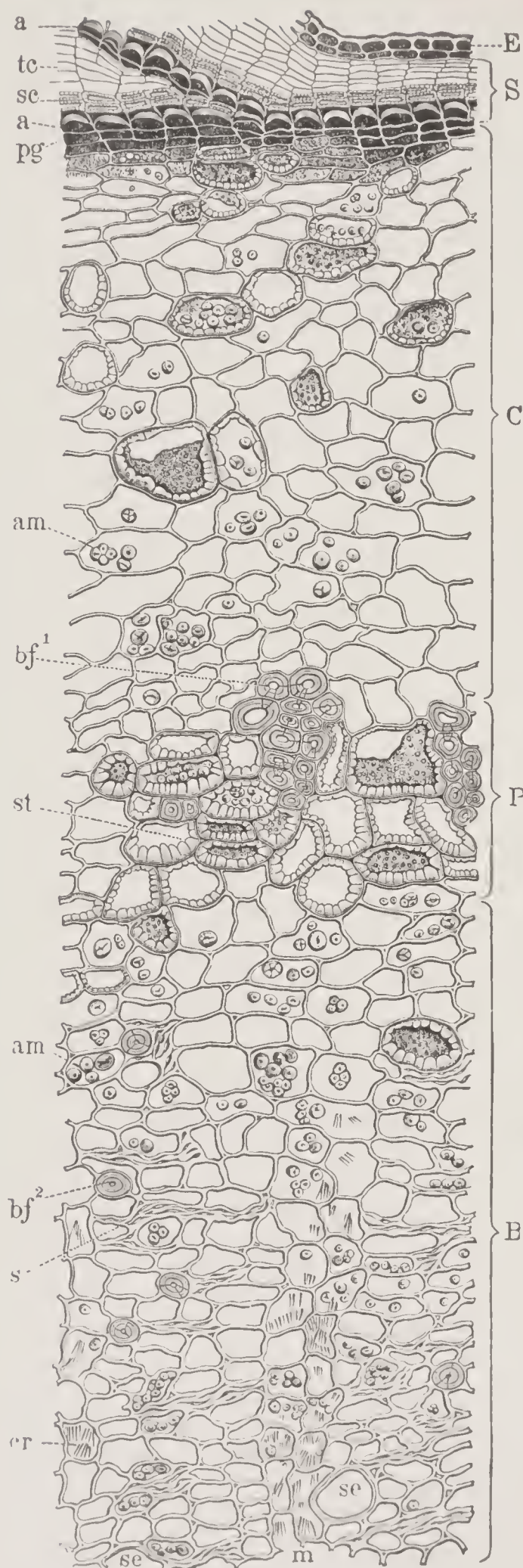
The common mode of shipment of the better grades is in bundles packed in small "mats."

Broken China cassia not only is in small pieces but often contains small twigs with wood as well as bark, also dirt, although the quality has much improved in recent years.

Because of its low pungency, ground China cassia is commonly reinforced by the addition of Saigon or Batavia cassia.

MACROSCOPIC STRUCTURE.—Although an inferior product, China cassia is seldom a thick bark, samples ordinarily being less than 3 mm. thick. The familiar long quills are rolled at the edges. Scraped quills are light brown with grayish spots where the scraper fails to remove all the outer coating.

MICROSCOPIC STRUCTURE (Figs. 48 and 49).—Cross sections cut through the gray spots show (1) *epiderm* (*E*) with a thick, colorless cuticle and dark contents; (2) *cork* (*S*) made up of phellogen (*pg*) the active layer, arch cells (*a*) with thick, bowed outer walls, stone cork (*sc*), and thin-walled cork (*tc*); (3) *cortex* (*C*) of ground parenchyma and stone cells, both containing numerous starch grains (*am*) and more or less brown matter; (4) *pericycle* (*P*) of stone cells (*st*) and bast fibers (*bf*¹), forming a zone interrupted by parenchyma cells with contents as in the cortex; and (5) *bast* or *phloem* (*B*) with ground parenchyma containing starch grains (*am*) and narrow crystals (*cr*), secretion cells (*se*), groups of collapsed sieve tubes (*s*), oc-



E occasional bast fibers (bf^2), and stone cells; the whole pierced by medullary rays (m).

The *cork* often splits up into two layers (Fig. 48, left) by the formation of a new phellogen.

A peculiarity of the *stone cells* of the cortex and pericycle is their thin outer wall.

C *Cassia starch* consists of rounded grains up to $22\ \mu$, with more or less distinct hilum and often clefts, and small aggregates, usually of two to four grains. With polarized light they show distinct but not brilliant crosses. The largest grains occur in the cortex and outer bast.

P Throughout the cortex and bast the cells contain a brown substance, soluble in dilute sodium hydroxide, which impregnates the walls. This in part is a product of the *secretion cells* which, however, are noticeable only in the bast. Stone cells and bast fibers stand out in striking contrast as the sclerenchymatized walls

FIG. 48.—China Cassia. Outer portion of medium thin bark in cross section. *E* epiderm with thick cuticle. *S* cork; *a* arch cells. *tc* thin cork, *sc* stone cork, *pg* phellogen. *C* cortex: thin-walled cells and stone cells with *am* starch grains. *P* pericycle: *st* stone cells. *bf¹* bast fibers. *B* bast (phloem): *s* sieve tubes, *bf²* bast fibers, *se* secretion cells, *m* medullary ray *am* starch grains, *cr* narrow crystals. $\times 160$. (A.L.W.)

do not take on the brown color. As is also true of cassia buds (which see), the secretion cells secrete in their thin walls volatile oil (which may harden to a resin) or mucilage, forming a swollen stratified mass brought out clearly in glycerin or potassium iodide-iodine mounts.

CHIEF STRUCTURAL CHARACTERS—Bark thin or medium, brown where scraped, flavor mild.

Pericycle, interrupted, of bast fibers and stone cells with thin outer wall, starch grains up to $22\ \mu$, secretion cells with oleoresin or mucilage; medullary rays with narrow crystals.

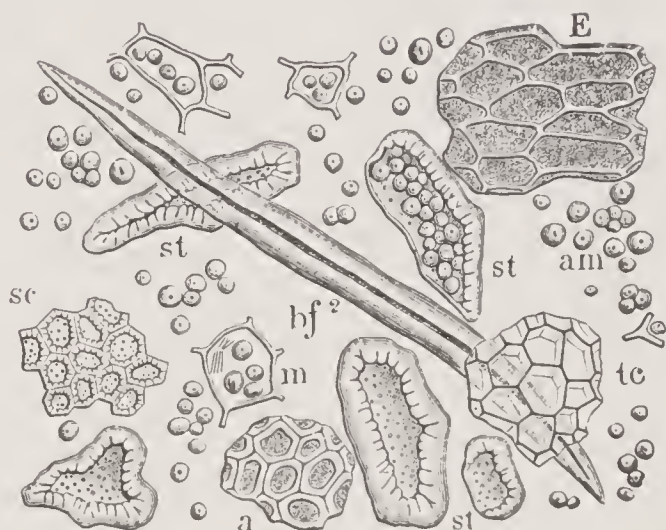


FIG. 49.—China Cassia. Elements of powder from medium thin bark. Reference letters as in Fig. 48. $\times 160$. (A.L.W.)

CHEMICAL COMPOSITION.—The analyses of cassia, cassia buds, and cinnamon by Richardson,¹ Winton, Ogden, and Mitchell,² and Sindall,³ given in the table on p. 264, were made by essentially the same methods.

Although in import trade cassia and cinnamon are sharply distinguished, in retail trade cassia is known as cinnamon. This usage has long been established, and the housewife, in the United States at least, is entirely unfamiliar with true cinnamon. China cassia is most commonly used for grinding, but to increase the pungency a certain amount of Batavia or Saigon cassia or cassia buds is often added.

The common impurities of whole cassia, such as wood and stems, find their way into the ground product. Formerly the product was often adulterated with sawdust, nut shells, cereal meal, biscuit colored with turmeric and iron oxide, linseed meal, exhausted cassia obtained in the distillation of the volatile oil, and other cheap materials.

The *U. S. Standards* include both cassia and cinnamon under the term cinnamon and limit, in the ground product, total ash to 5 per cent and sand to 2 per cent.

Fixed Oil.—The non-volatile ether extract or fixed oil consists chiefly of resinous matter not carefully investigated.

¹ U. S. Dept. Agr., Div. Chem. 1887, Bul. 13, II, 129.

² Connecticut Agr. Exp. Sta. Rep. 1898, p. 184.

³ J. Ind. Eng. Chem. 1912, 4, 590.

COMPOSITION OF CASSIA, CASSIA BUDS, AND CINNAMON

	Water	Protein	Oil, fixed	Oil, volatile	Alcohol extract	Crude starch*	Fiber	Ash, total	Ash, soluble	Sand
	%	%	%	%	%	%	%	%	%	%
<i>Cassia:</i>										
Saigon:										
Richardson...	9.32	4.55	2.38	3.51	16.95	5.86
W., O. and M.										
Min.....	6.53	3.63	2.34	2.43	3.92	18.36	17.31	4.17	1.64	0.08
Max.....	9.12	5.06	4.13	5.15	9.16	25.38	28.80	6.20	2.52	0.98
Aver. (8)...	7.64	4.18	2.87	4.04	6.60	21.83	23.88	5.23	2.06	0.37
Sindall.....	4.13	3.39	7.80	25.29	3.77	1.25	0.05
Batavia:										
Richardson...	17.45	4.03	0.74	0.55	14.33	5.25
W., O. and M.										
Min.....	8.65	4.50	1.32	1.23	11.00	16.65	17.03	4.04	1.49	0.02
Max.....	10.16	5.44	1.51	2.61	16.74	26.95	22.09	5.12	1.90	0.06
Aver. (6)...	9.33	4.99	1.43	1.99	13.50	21.55	20.19	4.58	1.72	0.04
Sindall										
No. 1.....	2.95	2.45	9.07	13.33	2.92	0.71	0.09
Good.....	4.10	2.49	9.38	14.08	4.10	1.67	0.19
China:										
Richardson...	11.04	2.63	1.86	1.21	15.45	2.48
W., O. and M.										
Min.....	10.87	3.31	1.56	0.93	4.57	20.57	23.08	3.01	0.71	0.10
Max.....	11.91	4.56	2.27	1.64	7.80	32.04	26.83	5.58	1.58	2.42
Aver. (6)...	11.27	3.89	1.80	1.31	5.32	27.08	24.51	4.21	1.14	1.32
Sindall										
Min.....	2.58	0.90	3.76	18.61	2.62	0.64	0.15
Max.....	4.45	2.71	8.86	24.84	3.96	1.45	1.24
Aver. (4)...	3.32	1.60	6.64	22.30	3.21	0.96	0.48
Corintjie:										
Sindall										
No. 1.....	4.45	1.33	6.78	19.04	5.97	2.08	0.13
Coarse.....	3.52	2.23	5.24	28.16	3.14	1.09	0.48
<i>Cassia Buds:</i>										
Richardson...	4.79	7.00	5.21	3.59	8.60	5.58
W., O. and M.										
I.....	7.12	8.00	6.27	4.65	10.90	10.44	13.89	4.58	2.88	0.19
II.....	8.74	7.06	5.65	3.11	10.86	10.98	12.80	4.70	2.88	0.35
<i>Cinnamon:</i>										
Ceylon:										
Richardson...										
Min.....	5.40	2.98	1.58	0.82	16.18	3.40
Max.....	10.00	3.80	3.30	3.14	33.08	4.55
Aver. (3)...	7.41	3.53	2.15	1.67	24.96	3.88
W., O. and M.										
Min.....	6.54	3.25	1.35	0.72	9.97	16.65	34.38	4.16	1.40	0.02
Max.....	10.48	4.56	1.73	1.94	16.73	22.86	38.48	5.99	2.71	0.58
Aver. (7)...	8.33	3.82	1.48	1.47	12.88	19.81	35.78	4.88	1.83	0.12
Seychelles:										
Sindall										
I.....	1.87	0.66	9.16	49.49	4.08	2.54	0.29
II.....	1.99	0.70	9.72	44.66	5.49	2.73	0.07

* Reducing matter by direct inversion calculated as starch.

Volatile Oil.—By Von Fellenberg's chromic acid oxidation method, Zäch¹ obtained 1.5 to 4.3 per cent.

Although an admixture of the less pungent twigs and leaves with cassia bark would obviously be improper, the oil is valued according to its flavor and strength rather than according to the part of the tree from which it is derived.

The loss of a volatile oil from ground cinnamon stored in paper bags has been shown by Horváth² to reach in one year as much as 33 per cent. In closed containers the maximum loss was 8 per cent.

Physical and Chemical Values.—Following are the limits, as compiled from various sources, for commercial cassia oil believed to be pure, although not necessarily derived solely from the bark:

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Boiling point	Acid No.	Cinna- mal	Non-vol. residue	Sol. 80% alcohol
			°	°C.		%	%	vol.
Min...	1.050	1.585	−1	240	6	70	1
Max...	1.070	1.614	+6	260	20	90	8	2

The *U. S. Standards* designate the volatile oil from *C. cassia* Bl. as oil of cassia and that from *C. zeylanicum* Breyne as oil of cinnamon. In oil of cassia they require not less than 80 per cent of cinnamal (cinnamic aldehyde). In both cassia and cinnamon extracts they require not less than 2 per cent of the volatile oil.

Some have believed that during storage of the oil a large part of the cinnamal changes to cinnamic acid with consequent increase of the residue after evaporation or distillation. Schimmel & Co. in 1890, however, reported results indicating that after 12 months the residue was not increased beyond 7 per cent—a limit since generally accepted.

More recent experiments reported by A. Chiris³ would appear to extend the limit of residue to 11.8 per cent, if the oil is distilled at diminished pressure, and still higher, if distilled in the normal manner, with lowering of the cinnamal content to 70 per cent. The 165 to 175° fraction, amounting to 5 per cent, was found to be *o-methoxycinnamaldehyde* boiling (13 mm.) at 165 to 167° and melting at 44 to 45° C., which is characterized by its easy resinification.

¹ Mitt. Lebensm. Hyg. 1932, **23**, 156.

² Kísérletügyi Közlemények 1932, **35**, 114.

³ Parf. France 1924, **19**, 263.

Chalot¹ gives the following interesting figures for the volatile oil obtained by primitive methods of distillation, the species in all cases being *C. Cassia* Bl:

	Yield	Sp. gr. 15° C.	Total aldehydes
	%		%
I Bark.....	1.20	1.035	88.9
II Buds.....	1.70	1.026	92.0
III Pedicels.....	1.70	1.046	92.0
IV Leaves.....	0.54	1.056	93.0
V Twigs.....	0.20	1.055	90.0
VI Mixture of III, IV, and V.....	0.77	1.055	93.0

No evidence is offered as to what aldehydes are present, but it is assumed that the amounts of aldehydes other than cinnamaldehyde are relatively small.

Rolet² states that the bark from any part of the tree contains 80 to 90 per cent of cinnamal.

Constituents.—The chief constituent is *cinnamal*; minor constituents, as listed by Dodge and Sherndal³ and by Dodge,⁴ are *methyl ortho-coumaraldehyde*, *salicylaldehyde*, *benzaldehyde*, *methyl salicylaldehyde*, *cinnamyl* and *phenyl-propyl acetates*, *benzoic* and *salicylic acids*, a *liquid acid* of fruity odor, and *coumarin*.

Cinnamal, cinnamaldehyde, or cinnamic aldehyde, $C_6H_5 \cdot CH : CH \cdot CHO$, first identified by Dumas and Péligot,⁵ is stated to form at least 75 per cent of cassia oil and may exceed 90 per cent. It is a colorless or light yellow liquid, has a specific gravity at 15° C. of 1.04, and boils at 245 to 247° C. under ordinary atmospheric pressure with partial decomposition. Under diminished pressure or with steam, it may be distilled unchanged. It has the odor of cassia oil and is soluble in alcohol. On oxidation it forms benzaldehyde and benzoic acid, thus explaining the presence of these substances in cassia oil.

Cinnamal may be prepared from cassia oil by first precipitating

¹ *Parfum moderne* 1923, **16**, 141.

² *Ind. chim.* 1923, **10**, 123.

³ *J. Ind. Eng. Chem.* 1915, **7**, 1055.

⁴ *Ibid.* 1918, **10**, 1005.

⁵ *Ann.* 1834, **12**, 24.

the double sulphite by shaking an ether solution of cassia oil with a concentrated solution of sodium bisulphite, then decomposing the crystals, after washing with alcohol, with dilute sulphuric acid, and finally distilling *in vacuo*. It may be synthesized from benzaldehyde, acetaldehyde, or from calcium cinnamate and formate. The substance itself, as well as the oil containing it, is used as a flavor, a perfume in soap and toilet preparations, and to some extent as a medicine.

Cinnamyl (cinnamic) acetate, $C_6H_5 \cdot CH : CH \cdot CH_2O \cdot CO \cdot CH_3$, a substance of disagreeable odor and taste, was found by Sehimmel & Co.,¹ who also reported the probable presence of phenyl-propyl acetate and free *cinnamic acid*.

Methyl ortho-coumaraldehyde, $C_6H_4(OCH_3)CH : CH \cdot CHO$, first reported by Rochleder and Schwarz² under the name of cassia steroptene, was later identified by Bertram and Kürsten.³ These authors also synthesized the substance.

Carbohydrates. *Starch*.—See table above.

Pentosans.—Hanus and Bien found 8.68 per cent dry basis. See also Introduction to Part III.

Mineral Constituents.—As analyzed by Hehner,⁴ 2 samples of cassia, denominated *C. lignea* (I) and *C. vera* (II), contained respectively 1.84 and 4.08 per cent of ash, and 3 samples of Ceylon cinnamon 4.59 to 4.78 per cent of ash. Analyses of the ash follow:

	K ₂ O	Na ₂ O	CaO	MgO	Fe ₂ O ₃	MnO	P ₂ O ₅	SO ₃	SiO ₂	Cl	CO ₂	Sand
	%	%	%	%	%	%	%	%	%	%	%	%
Cassia:												
I.....	20.58	3.98	25.29	5.48	1.23	5.11	3.67	2.02	0.90	0.14	27.18	3.16
II.....	5.60	0.90	52.72	1.10	6.14	1.13	1.13	0.71	0.20	0.09	36.26	0.24
Cinnamon:												
Min.....	10.35	2.97	36.98	2.65	0.41	0.13	2.20	2.42	0.25	0.18	29.29	0.52
Max.....	16.70	4.65	40.39	3.86	0.78	0.97	3.52	2.84	0.31	0.76	32.40	1.09
Aver. (3)...	13.76	3.87	39.15	3.27	0.55	0.65	2.91	2.66	0.28	0.48	31.32	0.71

Calcium.—Hendrick,⁵ confirming an observation by Dyer, found that the calcium in the form of oxalate was less in cassia than in cinnamon, as shown by the following summary:

¹ Ber. Oct. 1889, p. 19.

² Ber. Acad. Wiss. Wien. June 1850.

³ J. prakt. Chem. 1895, [2], **51**, 316.

⁴ Analyst 1879, **4**, 223.

⁵ Ibid. 1907, **32**, 14.

	Samples	Ash, total	Ash, soluble	Sand	Calcium oxalate	CaO as oxalate	CaO in other forms
		%	%	%	%	%	%
Cassia:	5						
Min.	2.43	0.69	0.14	0.05	0.02	0.37
Max.	6.30	1.33	1.63	1.34	0.58	0.90
Cinnamon:	3						
Min.	5.12	0.88	0.11	3.37	1.47	0.36
Max.	7.29	0.96	0.29	6.62	2.90	0.48

The total lime (CaO) expressed in terms of percentage of the total ash ranged as follows: cassia 17.3 to 35.3; cinnamon 37.1 to 46.4; that is, less in cassia ash than in cinnamon ash, whereas in Hehner's analyses the lime content of cinnamon ash falls between the extremes of cassia ash.

C. lignea and *C. vera* in both Hehner's and Hendrick's analyses are here summarized together under cassia since these terms no longer are regarded of botanical or commercial significance.

CHEMICAL COMPOSITION OF OIL OF OTHER SPECIES.—

C. oliveri Bail. The bark of this species, known as Brisbane sassafras, yielded in experiments by Hargreaves¹ 2.5 per cent of oil with a specific gravity at 23° C. of 1.030 and a refractive index at 23° C. of 1.5165. It contained *pinene* 12 to 15, *d-camphor* 18 to 20, *safrole* 25 to 27, and *eugenyl methyl ether* 40 to 45 per cent. The leaf oil contained *pinene* (mixed probably with a little *phellandrene*) 25, *d-camphor* 60, and *phenols* etc. 15 per cent.

C. sintok Bl. The bark of this wild species grown in the Dutch East Indies yielded in the hands of Kariyone and Morotomi² 6 per cent of oil with the following values: specific gravity 15°/4° 1.0410; refractive index at 15° C. 1.5298; optical rotation at 15° -1.84° ; saponification number 11.34; total phenols by volume 84 per cent (boiling under a pressure of 3 mm. at 120 to 121°); and acid number 850. The constituents identified were *eugenol* 76.7, *cineol*, and a *sesquiterpene*.

C. glanduliferum Meissn. Rutovskii, Vinogradova, and Kolotov³ found in the oil from the leaves and twigs: yield of oil 0.85 per cent; specific gravity at 20°/4° 0.9217; refractive index at 20° C. 1.4705;

¹ J. Chem. Soc. 1916, 109, 751.

² J. Pharm. Soc. Japan 1928, 48, 563.

³ Arb. Chem. Pharm. Inst. Moskaus, 1925, 11, 118.

optical rotation 25.78° ; ester number, direct 26.55, after acetylation 75.25; and acid number 1.32.

C. Massoia Schewe. Examination of 2 samples of Papua Massoi bark oil gave respectively: ¹ yield of oil 6.0 and 6.3 per cent; specific gravity at $15^\circ/15^\circ$ 1.060 and 1.064; refractive index at 20° C. 1.534 and 1.536; optical rotation -0.90° and -0.34° ; phenols as eugenol 60 and 79 per cent. The second sample was estimated to contain eugenol 79, safrole 14, and terpenes etc. 7 per cent.

C. parthenoxylon Meissn. The same authors found in oil distilled in the Federated Malay States from the wood the following: specific gravity at $15^\circ/15^\circ$ 1.103; optical rotation 0° ; solidifying point $+10^\circ$ C.; ester number, direct 0.8, after acetylation 3.5; soluble in 3.5 volumes of 90 per cent alcohol. The oil was shown to consist principally of *safrole*.

BATAVIA CASSIA

Cinnamomum Burmanni Bl. (?)

Fr. Cannelle de Batave. Sp. Canela Batavo. It. Canelladi.

Ger. Batavia-Zimt.

In commercial value as well as content of volatile oil Batavia cassia is intermediate between China and Saigon. It comes into the market scraped, in long quills, and resembles China cassia in appearance, but has a large amount of mucilage that is manifest by the taste, the high percentage of alcohol extract, and the slimy mass obtained on treating the powder with water.

The cassia described by Micko,² although lacking in pungency, is closely allied if not identical with Batavia.

MACROSCOPIC STRUCTURE.—Like China Cassia.

MICROSCOPIC STRUCTURE.—As in thick Saigon cassia the *crystals* are broad; as in Ceylon cinnamon the *starch grains* are small, usually 6 to 8 μ . Characteristic are the numerous but small *mucilage cells* in which is located the mucilage that gives the product its peculiar flavor and influences the results of chemical analysis.

CHIEF STRUCTURAL CHARACTERS.—Bark scraped, resembling China cassia. Taste mucilaginous.

Mucilage cells numerous, starch small, crystals broad.

CHEMICAL COMPOSITION.—See China Cassia.

¹ Bul. Imp. Inst. 1925, 23, 421.

² Z. Unters. Nahr.-Genussm. 1900, 3, 305.

SAIGON CASSIA

Cinnamomum Loureirii Nees

Ger. Saigon-Zimt.

While a strictly botanical classification of all the commercial cassias is impossible with our present information, Saigon cassia is much more pungent than the other grades on the American market and has certain structural characters consistent with its classification as a distinct species. It possesses in

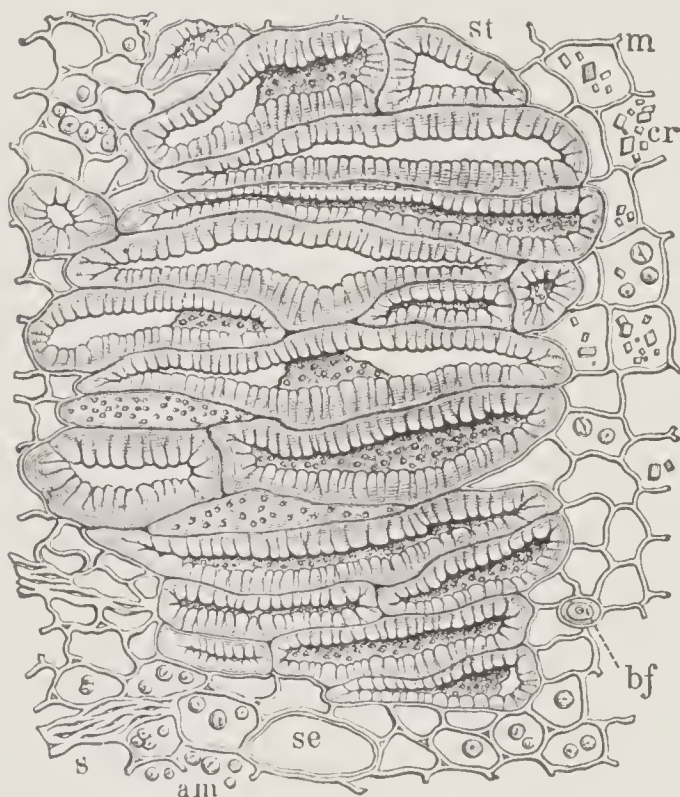


FIG. 50.—Saigon Cassia. Bast of thick bark in cross section. *st* stone cells; *bf* bast fibers; *se* secretion cells; *am* starch grains; *m* medullary ray with *cr* crystals; *s* sieve tubes. $\times 160$. (A.L.W.)

a high degree the cinnamon flavor which is very different in kind from that of true or Ceylon cinnamon. Its average content of volatile oil is fully twice that of Batavia cassia and three times that of China cassia. Even thick bark is highly pungent although somewhat less so than the thin.

MACROSCOPIC STRUCTURE.—In samples examined by the writers the unscraped bark varied from the thickness of writing paper up to 5 and even 10 mm. On the outer surface it is gray-brown with transverse and longitudinal wrinkles and wart-like scars. The end of thick bark, cut smooth with

a razor, when examined under a lens, shows the light-colored pericycle near the outer surface and light-colored rays of stone cells extending inward sometimes 2 mm. These are particularly prominent in quills that elsewhere on the cut surface are dark brown.

MICROSCOPIC STRUCTURE (Fig. 50).—Both thick and thin bark have larger (up to over $80\ \mu$) and usually more numerous secretion cells (*se*) containing volatile oil (*oleoresin cells*) than China or Batavia cassia. This is in accord with the higher content of volatile

oil. In other respects the structure of the thin and medium bark is not noticeably different from that of China cassia of like thickness.

Thick bark is characterized by tangentially elongated *stone cells* (*st*), arranged side by side in radial rows, extending inward into the phloem. These, unlike the pericycle stone cells of all other cassias examined, are not conspicuously thinner walled on the outer than the inner side.

The *bast fibers* of both thick and thin bark, also the *crystals* in the medullary rays of thin bark, are like those of China cassia, but the crystals in the medullary rays of thick bark are broad and more or less isodiametric.

CHIEF STRUCTURAL CHARACTERS.—Bark varying from paper-thickness to 10 mm. Flavor highly pungent.

Secretion cells larger and more numerous than in other cassias; otherwise thin bark structurally like China cassia; thick bark with large radial groups of tangentially elongated stone cells and broad, isodiametric crystals.

CHEMICAL COMPOSITION.—See China Cassia.

Volatile Oil.—The bark of the twigs was found by Rolet¹ to yield 0.2 per cent and of the roots 1.7 per cent of oil. The oil contained *aldehydes* 27 per cent and *linalool* 40 per cent, also *eugenol* and *eucalyptol*.

CEYLON CINNAMON

Cinnamomum zeylanicum Breyne

Fr. Cannelle de Ceylan. Sp. Canela. It. Cinnamomo.

Ger. Ceylon-Zimt.

True or Ceylon cinnamon is the bark of the young wood of the above species grown not only in Ceylon but in other parts of India and in the East Indies and more recently introduced into the West Indies, Mexico, and South America. Its flavor is so different from that of any of the cassias—a difference as marked as wintergreen from sassafras or spearmint from peppermint—as at once to suggest that the tree belongs to a distinct species. The flavor may be described as a combination of cassia and ealamus.

While cassia or its volatile oil is preferred for flavoring rolls, cake, pies, and confectionery, true cinnamon is more suitable for certain sauces and gravies, as well as cordials, imparting a peculiar, illusive flavor appealing to the epicure.

¹ Ind. chim. 1923, 10, 123.

The thin, scraped bark is made into composite sticks, a meter or more long and 5 to 10 mm. in diameter, by rolling a considerable number of pieces together. These sticks are made into bundles for shipment and broken up into smaller bundles for distribution.

MACROSCOPIC STRUCTURE.—The scraped *bark* on its outer surface is of a dull buff color with silky bast fibers evident under a lens.

It accordingly consists only of pericycle and bast.

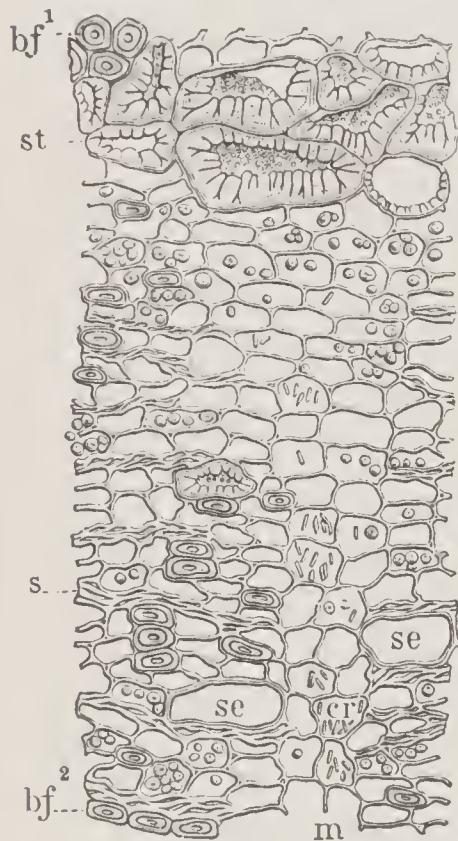


FIG. 51.—Ceylon Cinnamon. Outer part of quill in cross section. Pericycle: *bf*¹ bast fibers; *st* stone cells. Phloem: *s* sieve tubes; *se* secretion cells; *bf*² bast fibers; *m* medullary ray with *cr* crystals. $\times 160$. (A.L.W.)

MICROSCOPIC STRUCTURE (Fig. 51).—The *pericycle* of *stone cells* (*st*) and *bast fibers* (*bf*¹) is nearly like that of *cassia*. Moeller¹ notes that the ring of stone cells is more nearly closed. He also states that the stone cells are larger, more strongly and uniformly thickened, and that the bast fibers are narrower. Though these statements may be true in general, we find that the maximum dimensions in both barks are not noticeably different.

We confirm his findings that the *parenchyma* of cinnamon is of more delicate (smaller) cells than that of *cassia*, also that *bast fibers* occur in tangential and radial rows, at least in the bast, but these distinctions are of little service in the diagnosis of the powder.

A more useful distinction is the greater number of *bast fibers* in cinnamon and the smaller size of the *starch grains* which Moeller states as a rule are about 6 μ and seldom reach double that size. Vogl,² however, found no appreciable difference in the size of the starch grains. It is probable that such difference as exists is due more to the fact that the cortex, which in general contains larger starch grains than the phloem, has been removed from cinnamon.

The complete absence of *cork tissues* in cinnamon is especially worthy of notice. The *crystals* in the medullary rays are narrow.

¹ Mikros. Nahr.-Genussm., Berlin, 2 Aufl. 1905, p. 518.

² Wicht. Nahr.-Genussm., Berlin, 1899, p. 512.

CHIEF STRUCTURAL CHARACTERS.—Bark scraped, thin, buff, with bast fibers on surface, in compound quills. Flavor a combination of cassia and calamus.

Cork absent. Bast fibers (in rows) more numerous, starch grains smaller, parenchyma smaller-celled than in cassia. Medullary crystals narrow.

MICROSCOPY OF GROUND CINNAMON.—The presence of certain foreign barks in ground cinnamon would present a difficult problem for the microscopist; such an addition, however, has never been encountered by the writers. Ground cocoanut shells and biscuit made from refuse and colored with iron oxide were at one time common adulterants. The first is detected by the stone cells and the latter by the distorted starch grains and the bran tissues.

CHEMICAL COMPOSITION.—Proximate analyses are given under Cassia.

Beythien and Hepp¹ in a sample of Seychelles cinnamon ground by them found: volatile oil 0.42, crude starch 6.9, fiber 47.05, and ash 6.69 per cent—all indicative of low grade. The following more extensive analysis of Seychelles cinnamon is by Rosenthaler and Reis²: water 9.38, protein 2.04, total ether extract 4.20, volatile ether extract (volatile oil) 2.83, cinnamaldehyde 1.33, alcohol extract 7.27, water extract 6.52, fiber 36.04, total ash 8.60, water-soluble ash (dry basis) 1.07, and sand 0.44 per cent; alkalinity of ash (cc. normal acid per 100 grams of sand-free dry substance) 24.7.

Meyer³ gives the following results on a sample of Seychelles cinnamon: oil of cinnamon 1.12 (containing aldehydes 71.2 and eugenol 15.8), alcohol extract 10.37, fiber 38.1, total ash 5.50, and sand 0.10 per cent.

Volatile Oil.—Cinnamon bark oil contains less cinnamal than cassia bark oil. Unlike the latter it has a notable amount of eugenol. The leaf oil consists largely of eugenol, hence the term cinnamon oil should be restricted to the product of the bark, containing none from the leaves. Zäch,⁴ by the Von Fellenberg chromic acid oxidation method, obtained 1.5 to 3.0 per cent from the bark.

Physical and Chemical Values.—Cinnamon Bark Oil. Hill⁵ and

¹ Z. Unters. Nahr.-Genussm. 1910, **19**, 367.

² Ber. pharm. Ges. 1910, **19**, 490.

³ Arb. kais. Gesundh. 1911, **36**, 372.

⁴ Mitt. Lebensm. Hyg. 1932, **23**, 156.

⁵ Chem. and Drug. 1910, **76**, 59.

Umney and Bennett¹ obtained lower results on specific gravity, refractive index, and aldehydes in cinnamon oil than in cassia oil. This difference is not so strongly marked in results given by Schimmel & Co., Parry, Gildemeister and Hoffmann,² and other authors.

The following values cover both Ceylon and Seychelles oil, the lower figures for physical values and aldehydes applying chiefly to the latter:

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Cinna- mal	Eugenol	Sol. 80% alcohol
			°	%	%	vols.
Min.	1.006	1.571	−4	63	4	2
Max.	1.040	1.608	0	84	12	3

In the bark oil from old and young branches, Pilgrim³ found respectively 50 and 70 to 75 per cent of aldehydes.

In the examination made at the Imperial Institute⁴ of the bark from the Gold Coast, the heavy oil separated by gravity from the aqueous portion of the distillate gave: yield of oil 1.18 per cent, specific gravity 1.042, refractive index 1.603, and aldehydes 86 per cent. The light oil extracted by ether from the aqueous portion amounted to 0.3 per cent and when added to the heavy oil reduced the aldehyde content to 68 per cent.

According to analyses reported by Roure-Bertrand fils,⁵ cinnamon oil separated from pounded Madagascar bark is quite different from that extracted from the aqueous layer by petroleum ether, the values of these, as well as of the mixed oils, being respectively: specific gravity at 15° C. 0.973, 1.030, and 1.009; optical rotation at 16 to 17° C. −5.6°, −2.0°, and −3.0°; acid number 2.49, 2.49, and 2.49; aldehydes 48, 82, and 70 per cent; and solubility in 70 per cent alcohol, insoluble, 0.75 volume, and 2 volumes.

Cinnamon Leaf Oil. The following are the values of the oil from the leaves of Ceylon cinnamon:

¹ Ibid. 1910, **77**, 198; Perf. Ess. Oil Rec. 1910, **1**, 169.

² Ätherischen Öle, Leipzig, 3 Aufl. 1929, **2**, 610.

³ Pharm. Weekbl. 1919, **56**, 50.

⁴ Bul. 1918, **16**, 147.

⁵ Sci. ind. bul. 1921 [4], **4**.

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Sol. 70% alcohol
Min.	1.044	1.5330	° -0.5	vols. 1.5
Max.	1.065	1.5400	+1.3	3

Leaf oil from Seychelles cinnamon, as given in the Bulletin of the Imperial Institute,¹ showed: specific gravity at 15°/15° 1.0488, refractive index at 20° C. 1.533, optical rotation at 20° -2.06°, eugenol 86 per cent, aldehydes (bisulphite method) 3 per cent, soluble in 1.5 volumes of 70 per cent alcohol at 15°. As given by A. Chiris² the values of leaf oil from Mayotta are: specific gravity at 15° C. 1.050; refractive index at 20° C. 1.5390; saponification number 81.2; eugenol (3 per cent soda) hot 79.5, cold (with solvent) 58.0 per cent; and soluble in 1.8 volumes of 70 per cent alcohol.

Cinnamon Root-Bark Oil. The light yellow oil examined by Pilgrim showed: specific gravity at 15° C. 0.993 and optical rotation at 20° +50.2° (200-mm. tube).

Constituents.—Cinnamon Bark Oil. The presence of *cinnamal* in cinnamon oil (up to 65 per cent), as well as in cassia oil, was shown by Dumas and Péligot.³ *Eugenol* is present in amounts ranging from 4 to 8 per cent.

Walbaum and Hüthig⁴ and other chemists with Schimmel & Co.⁵ identified in the oil from Ceylon bark the following minor constituents: three terpenes, namely *l-phellandrene*, *l- α -pinene*, and *caryophyllene*; *cymene*; five aldehydes, namely *benzaldehyde*, *phenyl-propyl aldehyde*, *nonylaldehyde*, *cuminaldehyde*, and *furfural*; *l-linaloöl*; *linallyl isobutyrate*; and *methyl n-amylketone*.

In Seychelles bark oil, Fritzsche Brothers⁶ found *cinnamal*, *eugenol*, another *phenol*, *caryophyllene*, *β -phellandrene*, *cymene*, and *camphor*. In a later report⁷ they add *camphene*, *β -pinene*, *l-limonene*, *nonylaldehyde*, *benzaldehyde*, and (tentatively) *linaloöl*.

¹ 1924, **22**, 265.

² Parf. France 1924, **16**, 152.

³ Ann. 1834, **57**, 305.

⁴ J. prakt. Chem. 1902 [2], **66**, 47.

⁵ Rep. Oct. 1892, 47; Apr. 1902, 14.

⁶ Schimmel & Co. Rep. Nov. 1908, 41.

⁷ Apr. 1913.

Cinnamon Leaf Oil. Stenhouse¹ reported 70 to 90 per cent of *eugenol*. *Safrole*, *benzaldehyde*, *terpenes*, and *linaloöl* have also been found in small amount. It is a curious fact that cinnamal has been detected only in negligible quantity in true cinnamon leaf. In the dried leaves of Padang cinnamon (*Cinnamomum burmanni*), however, Rowaan² found 0.4 per cent of volatile oil containing 45 to 62 per cent of *cinnamaldehyde* with probably only about 10 per cent of *eugenol*.

Cinnamon Root-Bark Oil. The chief constituent found by Pilgrim³ was *camphor*; others present were *pinene*, *cineol*, *dipentene*, *phellandrene*, *eugenol*, *safrole*, probably *caryophyllene*, and possibly *borneol*. Only small amounts of esters and aldehydes (cinnamal doubtful) were present.

Eugenol and *caryophyllene* are described under Cloves.

Pentosans.—In dry matter 13.63 per cent. See also Introduction to Part III (Hanus and Bien).

Mineral Constituents.—See Cassia.

SASSAFRAS

Sassafras variifolium Kuntze = *S. officinale* Nees = *Laurus Sassafras* L.

Fr. Sassafras. Sp. Sassafras. Ger. Sassafras.

A popular flavor for beverages and candies in the United States is obtained from the root bark and in lesser amount from the root wood of a native tree. The combined flavor of sassafras and sweet birch, also a product of an American tree, is known as sarsaparilla.

CHEMICAL COMPOSITION.—The wood and inner bark of the young wood changes to a reddish orange color on exposure to the air. The red color named *sassafrid* by Reinsch⁴ and the *sassafrin* and *sasarubin* of Hare⁵ have not been thoroughly studied.

Volatile Oil.—The root bark contains as much as 9 per cent of volatile oil, the root wood about 1 per cent.

¹ Ann. 1855, **93**, 269.

² Chem. Weekbl. 1936, **33**, 698.

³ Loc. cit.

⁴ Jahresb. 1845, **31**; 1846, **36**.

⁵ Am. J. Pharm. 1837.

Physical and Chemical Values.—The following limits, including hydrogen number by Albright,¹ apply to sassafras oil:

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Ester No.	Acid No.	Hydrogen No.	Sol. 90% alcohol
			°				vols.
Min.	1.065	1.520	+2	0.5	102.0	1
Max.	1.095	1.530	+4	5.0	1	103.1	2

Constituents.—Power and Kleber² state that 80 per cent of the oil is *safrole* which separates on cooling. The other constituents found are *pinene* and *phellandrene* 10, *d-camphor* 6.8, *eugenol* 0.5, and *sesquiterpenes* and residue 3 per cent.

Safrole, $C_{10}H_{10}O_2$ or $C_6H_3(CH_2 \cdot CH : CH_2)(O_2CH_2)$, appears to be identical with the shikimol of Eijkman obtained from the fruit of shikimi. Grimaux and Ruotte³ first obtained its empirical formula. Its physical values are: specific gravity at 15° C. 1.108, melting point +8° C., and boiling point 231 to 233° C. The hydrogen number, according to Albright,⁴ is 135.6. Heated with alcoholic soda, it passes into its isomer *isosafrole* with $CH_2 \cdot CH : CH_2$ changed to $CH : CH \cdot CH_3$ and the optical rotation to -18° . The constitution of the two substances was determined by Eijkman,⁵ Poleck,⁶ and Poleck and Thümel.⁷

Cajola⁸ names the terpene *safrene*, the phenol ester *safrole*, an alcohol, and a volatile phenol-like substance as constituents of the root oil.

¹ J. Am. Chem. Soc. 1914, **36**, 2188.

² Pharm. Rundsch. 1896, **14**, 101.

³ Compt. rend. 1869, **68**, 928.

⁴ Loc. cit.

⁵ Ber. 1885, **18**, 281R.

⁶ Ibid. 1886, **19**, 1094.

⁷ Ibid. 1889, **22**, 2863.

⁸ Riv. ital. ess. profum. 1930, **12**, XXII.

FLOWER SPICES

AMONG full-blown flowers the violet and among parts of flowers rose leaves and saffron are here described. Cloves and capers are flower buds.

FLOWER STIGMAS OF THE IRIS FAMILY

(*Iridaceæ*)

THE species described below serves as both spice and coloring. Stigmas of other species are worthless. Certain substitutes are whole flowers, not stigmas.

SAFFRON

Crocus sativus L.

Fr. Safran. Sp. Azafran. It. Zafferano. Ger. Safran.

The stigmas of the above species, a native of Persia, Asia Minor, and Greece, constitute the saffron of commerce. In addition to the countries named, the plant is cultivated in France, Spain, and Italy. It is closely related to the crocus of the flower garden (*C. vernus* L.), but the stigmas of the latter are worthless as a dye, a spice, or a drug.

Before the advent of coal-tar dyes, saffron was much in demand as a dyestuff, but now it has gone the way of natural indigo and madder. As a spice and drug it is now little used and in the United States is almost unknown.

The stigmas are picked by hand by women and children, the labor item alone making the cost of the product at the present time prohibitive.

Because of its high cost, adulteration has been common. Among the substitutes are flowers of safflower (*Carthamus tinctorius* L.), with slender corolla tube and five narrow lobes; marigold (*Calendula officinalis* L.), with strap-shaped corolla, narrow at the base; Cape saffron (*Lyperia crocea* Eckl.), with long corolla tube and five round lobes; South African saffron (*Tritonia aurca* Pap.), with cylindrical corolla, funnel-shaped at the end; and other species, also red sandal-

wood, corn silk, and various materials colored with coal-tar dyes. Weighting materials have also been added.

MACROSCOPIC STRUCTURE (Fig. 52).—The *stigmas*, three in number, are borne on a slender *style*. They range up to 3 cm. long and are commonly described as trumpet-shaped, although slit on the inner side and scalloped at the extremity. The styles are yellow, the stigmas red.

MICROSCOPIC STRUCTURE (Fig. 53).—*Elongated cells*, long (pa^1) and short (pa^2) *papillæ*, and delicate *fibro-vascular bundles* make up the tissues.

Rounded *pollen grains*, some with tubes passing into the body of



FIG. 52.

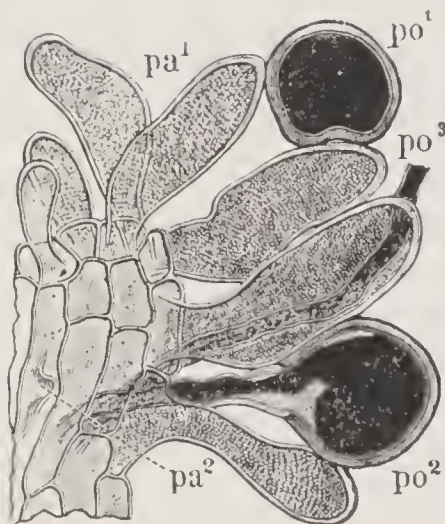


FIG. 53.

FIG. 52.—Saffron. $\times 1\frac{1}{2}$. (A.L.W.)

FIG. 53.—Saffron. Tip of stigma: pa^1 long papillæ; pa^2 short papilla; po^1 pollen grain; po^2 pollen with tube extending into stigma; po^3 pollen tube. $\times 160$. (A.L.W.)

the stigma between the papillæ, are often lodged among the papillæ.

Treated with concentrated sulphuric acid the deep red coloring matter changes first to blue and then to brown.

CHIEF STRUCTURAL CHARACTERS.—Stigmas three, trumpet-shaped, scalloped at end, red; styles yellow.

Cells elongated throughout; papillæ present on epiderm; vascular bundles slender. Pollen grains round.

CHEMICAL COMPOSITION.—The results obtained by Arnst and Hart¹ are believed to represent fairly the genuine product, except that figures for reducing sugars, about 20 per cent, are not included.

¹ Z. angew. Chem. 1893, No. 5, 136.

COMPOSITION OF SAFFRON (ARNST AND HART)

	Water	Protein	Oil, fixed	Oil, volatile*	N-f. ext.	Starch equiv.†	Fiber	Ash
	%	%	%	%	%	%	%	%
Spanish.	15.90	12.57	4.69	0.81	57.30	11.99	4.88	4.05
Italian..	14.45	13.58	8.57	0.37	54.39	12.51	4.38	4.26

* Volatile ether extract. † Reducing matter, other than sugars, by direct inversion, calculated as starch.

Analyses of pure and adulterated saffron are given by Parkes.¹

Kuntze and Hilger² in 30 samples of saffron found a range of 8.89 to 16.82 per cent of water and of 4.48 to 6.90 per cent of ash. Beythien³ in 120 samples reports a range of 5.01 to 12.26 per cent of water. Of 112 samples there was only 1 with over 8 per cent of ash.

Pierlot⁴ in 40 samples of known purity found a range of from 2.22 to 2.44 per cent of nitrogen equivalent to 13.88 to 15.25 per cent of protein. He considers, however, that the nitrogen is largely in the form of lecithins. In a later paper⁵ he shows that added sugar may be detected by determining the reducing power of a cold water extract before and after inversion, and added sodium sulphate, as well as other foreign mineral substances, by determining the ash and ash constituents. The sugar and sodium salt are added in the form of solution which impregnates the tissues.

The maximum limits of the *U. S. Standards* are yellow styles and other foreign matter 10 per cent, loss at 100° C. 14 per cent, total ash 6 per cent, and sand 1 per cent.

Volatile Oil.—By Von Fellenberg's chromic acid oxidation method, Zäch⁶ obtained 0.6 to 1.0 per cent.

Physical and Chemical Values.—According to Pierlot,⁷ who examined the oil obtained by steam distillation of the ether extract, the specific gravity at 15°/15° ranges from 0.9514 to 0.9998 and the optical rotation is slightly to the left. Weiss⁸ gives the boiling point as 209° C.

¹ Pharm. J. 1908, 80, 267.

² Arch. Hyg. 1888, 8, 468.

³ Z. Unters. Nahr.-Genussm. 1910, 19, 365.

⁴ Ann. fals. 1916, 9, 24.

⁵ Ibid. 1923, 16, 215.

⁶ Mitt. Lebensm. Hyg. 1932, 23, 156.

⁷ Chim. Ind. 1925, 14, 839.

⁸ J. prakt. Chem. 1867, 101, 65.

Constituents.—Weiss found that the oil contains oxygenated constituents. Kayser¹ reports the presence of *picrocrocine* ($C_{38}H_{66}O_{17}$), a bitter substance, which hydrolyzes on boiling with dilute acid to three molecules of crocose ($C_6H_{12}O_6$) and two of a terpene ($C_{10}H_{16}$). The same terpene is stated to occur free. Kayser's picrocrocine melted at 75° C.; Pierlot, however, on recrystallization secured crystals melting at 196° C., indicating that Kayser did not obtain a pure substance. Pierlot hydrolyzed picrocrocine to (1) sativol, (2) an amorphous lactone compound evidently a phthalein, (3) fructose, and (4) formic acid.

Pierlot observed that a *stearoptene*, melting after recrystallization from ether and petroleum ether at 106° C., deposits from the oil on standing. Rectification *in vacuo* yielded pure *sativol*. This substance is apparently a tertiary alcohol since it responds to Denigès' mercuric sulphate reaction. On dehydration it yields a liquid hydrocarbon. Its specific gravity at 15° is 0.9681, its boiling point at 760 mm. is 217°, its optical rotation is 0.

Carbohydrates.—Biological tests by Wattiez² indicated the presence of 1.0 to 1.5 per cent of an *unknown sugar* hydrolyzable by invertase.

Pfyl and Scheitz³ call attention to the presence of a chloroform-soluble *glucoside* yielding on inversion fructose which is determined by copper reduction.

Pure saffron, according to Zäch,⁴ should contain as follows: aqueous extract, whole 58 to 62, ground 61 to 65; reducing matter before inversion 22 to 25, after inversion 24 to 27 per cent.

Pentosans.—Hanus and Bien found 5.20 per cent, dry basis. See Introduction to Part III.

Colors.—Huss⁵ determined the color value of a 0.1 per cent solution in 65 per cent alcohol in terms of percentages of 1.5 per cent potassium dichromate solution. The maximum value found was 1.5 per cent; the usual range, 1.0 to 1.2.

Crocin or polychroit, $C_{44}H_{70}O_{28}$, according to Kayser⁶ is the yellow coloring substance of saffron. In its preparation the defatted material is exhausted with cold water and the liquid is shaken with ani-

¹ Ber. 1884, 17, 2228.

² J. pharm. Belg. 1928, 10, 371.

³ Z. Unters. Nahr.-Genussm. 1908, 16, 337.

⁴ Mitt. Lebensm. Hyg. 1933, 24, 156.

⁵ Tek. Tid. 1922, 52, 565.

⁶ Loc. cit.

mal charcoal which absorbs the color. After the charcoal is dried, the color is extracted with 90 per cent alcohol from which it is obtained by evaporation as a brown-yellow odorless substance with a sweetish taste. It is very slightly soluble in ether but readily in water and alcohol. With concentrated sulphuric or nitric acid it forms a blue coloration changing respectively to violet and yellow. Hydrolyzed with dilute acid it yields crocetin and *d*-glucose.

Crocetin, according to Kayser,¹ is a dark red substance soluble in alcohol and ether, but nearly insoluble in water, differing from crocin in that it is precipitated by lime or baryta water and lead subacetate. He considered it to have the formula $C_{34}H_{46}O_9$; Karrer, Benz, Morf, Raudnitz, Stoll, and Takahashi,² however, assign to it the following formula showing relationship to carotene (see Introduction to Vegetables, Volume II):



Hordh³ considers that saffron should contain not less than 8 per cent of crocetin.

Enzymes.—*Emulsin*, capable of acting on a glucoside present in saffron, was found by Wattiez.⁴

Mineral Constituents.—Kuntze and Hilger⁴ give partial ash analyses which, recalculated, follow:

	K ₂ O	Na ₂ O	P ₂ O ₅	SO ₃	Cl
	%	%	%	%	%
Saffron.....	34.46	8.56	10.01	7.12	1.89
Safflower.....	1.47	5.11	4.91
Calendula.....	37.69	9.56	0.27	3.29	8.94

Minor Mineral Constituents. *Boron.*—Krizan⁵ has shown that boron is a normal constituent of the ash.

¹ Loc. cit.

² Helv. Chim. Acta 1932, **15**, 1218.

³ Anal. asocn. quím. Argentina 1934, **22**, 45.

⁴ Loc. cit.

⁵ Boll. chim. farm. 1914, **53**, 10.

FLOWERS OF THE CAPER FAMILY

(*Capparidaceæ*)

A SINGLE species yields capers. Flower buds of other species are sometimes substituted.

CAPERS

Capparis spinosa L.

Fr. Câpres. Sp. Alcaparra. It. Cappero. Ger. Kapern.

True capers are the flower buds of a sprawling, spiny shrub, a native of southern Europe and northern Africa. The caper shrub is cultivated in rocky but sunny regions of France, Spain, Italy (especially Corsica and Sicily), Greece, and various islands of the Mediterranean. The Riviera east of Marseilles produces capers of recognized excellence.

After picking, the flower buds are allowed to wilt, then packed for shipment in casks with salt and vinegar. Finally they are repacked in bottles.

According to Hanausek ¹ common substitutes are the flower buds of Scotch broom (*Spartium scoparium* L., *Sarothamnus scoparius* Wimm.), known as German capers, the flower buds and green fruits of the garden nasturtium (*Tropæolum majus* L.), the flower buds of marsh marigold (*Caltha palustris* L.), and (in England) the poisonous fruits of the caper spurge (*Euphorbia lathyris* L.).

MACROSCOPIC STRUCTURE (Fig. 54).—The four *sepals* are rather thick, leathery, spotted, and spurred at the base, the opposite outer pair overlapping the inner pair (I and II). After carefully expanding the bud, the four thin, rounded, saucer-shaped *petals*, the numerous *stamens*, and the stalked *ovary* with sessile stigma are clearly seen (III). The mottling of the sepals varies greatly, some being mostly light gray, often pink at tip, with spots of dark green, others mostly dark green with light markings occurring chiefly on the veins and edges.

Hanausek ¹ notes that the stalk of the ovary is twisted.

¹ Nahr.-Genussm. Kassel, 1884, p. 263.

MICROSCOPIC STRUCTURE (Fig. 55). **Calyx.**—The *outer epiderm* (*eps*) consists of polygonal cells and stomata, both with striated cuticle. Some of the cells are filled with contents which under the microscope are darker than the others. Strange to say these are the cells which are light-colored to the naked eye, the opaque contents reflecting the light. It is probable that the material contained in these cells is largely the glucoside *rutin*, a crystalline substance becoming bright yellow with alkali. Hanausek¹ states that the rutin ($C_{25}H_{28}O_{15}$) is secreted in subepidermal glands, furthermore that it



FIG. 54.

FIG. 54.—Capers. I top. II side. III expanded. $\times 2$. (A.L.W.)

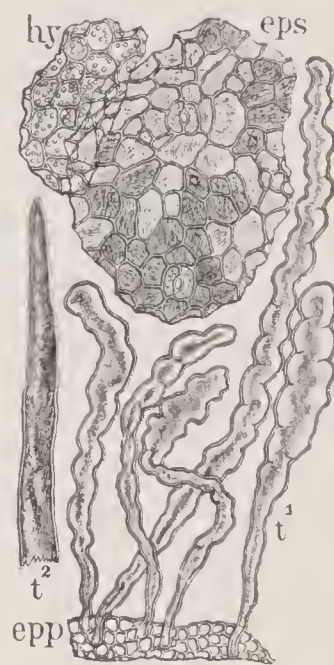


FIG. 55.

FIG. 55.—Capers. *eps* outer epiderm of sepal (cells containing rutin, dark) and *t*² hair from base; *hy* hypoderm with chlorophyll grains. *epp* epiderm from edge of petal with *t*¹ intestine-like hairs. $\times 160$. (A.L.W.)

occurs also in the leaves of *Ruta graveolens* L. and the yellow berries and the flower buds of *Sophora japonica* L.

Long, thin-walled, pointed *hairs* (*t*²) occur at the base of the calyx.

The *hypoderm* (*hy*) and *mesophyl* contain rounded chlorophyll grains.

Striations are lacking on the *inner epiderm* which otherwise resembles the outer epiderm.

Corolla.—Characteristic are the curious long, club-shaped *hairs* (*t*¹) with intestinelike convolutions, arising from among the minute cells at the edge (*epp*).

¹ Loc. cit.

CHIEF STRUCTURAL CHARACTERS.—Flower buds with four mottled sepals, four petals, numerous stamens, and stalked ovary.

Outer epiderm of sepals of polygonal cells, some containing rutin. Edge of petals with club-shaped, convoluted hairs.

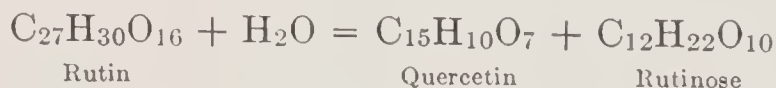
CHEMICAL COMPOSITION.—Analyses of the salted and pickled capers have been made by Arnst and Hart.¹ Judging from the high ash and low protein, as well as the high chlorine content of the ash, the first and second analyses in the table are of capers packed in brine of high salt content.

COMPOSITION OF CAPERS (ARNST AND HART)

	Water	Protein	Fat	N-f. ext.	Fiber	Ash
	%	%	%	%	%	%
Salted:						
Nonpareilles	87.20	2.70	0.56	4.85	1.25	3.44
Capotes	88.52	2.61	0.51	4.59	1.23	2.54
Pickled:						
Superfines	87.54	3.61	0.48	5.60	1.43	1.34
Capucines	86.40	3.96	0.53	6.52	1.47	1.12

Glucosides. *Rutin*, $C_{27}H_{30}O_{16}$.—The formula here given is that assigned to this glucoside by Schmidt² and accepted by Charaux.³ Various other formulas have been proposed, such as $C_{25}H_{28}O_{15}$ by Zwenger and Dronke and $C_{33}H_{42}O_{20}$ by Ter Meulen.

The glucoside may be isolated from pickled capers by extracting with hot water after washing with cold water to remove salt and vinegar. The fine yellow needles melt at about 190° C. and give an intense green color with ferric chloride. As shown by Schmidt,² on boiling with acid, rutin breaks down into rhamnose, dextrose, and quercetin. According to Charaux,³ hydrolysis by the enzyme rutinase yields quercetin and a new sugar rutinose, the reaction being as follows:



By acid hydrolysis, rutinose and one molecule of water form equal molecules of rhamnose ($C_6H_{12}O_5$) and dextrose.

¹ Z. angew. Chem. 1893, 6, 136.

² Arch. Pharm. 1904, 132, 210.

³ Compt. rend. 1924, 178, 1312.

Pentosans.—In dry matter 4.01 per cent. See also Introduction to Part III (Hanus and Bien).

Mineral Constituents.—Determinations have been made by Arnst and Hart ¹ on the samples, analyses of which are tabulated above:

	K ₂ O	Na ₂ O	CaO	MgO	P ₂ O ₅	SO ₃	Cl
	%	%	%	%	%	%	%
Salted:							
Nonpareilles.	8.27	37.46	5.07	1.36	2.30	3.05	47.82
Capotes.	12.50	31.06	7.34	2.24	2.66	4.22	39.80
Pickled:							
Superfines. . .	20.62	8.50	17.91	3.51	9.87	23.04	14.00
Capucines. . .	20.30	2.14	9.04	2.32	13.34	21.74	6.04

¹ Loc. cit.

PETALS OF THE ROSE FAMILY

(*Rosaceæ*)

VARIOUS species of *Rosa* yield oil of rose, primarily of value as a perfume.

ROSE

Rosa spp.

Fr. Rose. Sp. Rosa. It. Rosa. Ger. Rose.

Although the petals are candied and used to a limited extent as a confection, the rose is of chief interest in connection with the distillation of the volatile oil, attar (otto) of roses, an important industry in Bulgaria. The oil is also prepared to some extent in Germany, France, and Austria. A number of species are grown for this purpose but the principal one is *R. damascena* Mill. and its variety *trigintipetala* Dieck. Among those less frequently used are *R. centifolia* L. and *R. alba* L.

In dilute alcoholic solution the oil is of great importance in the perfumery and cosmetic industry. It also furnishes a desirable flavor for cake, pastries, candies, and cordials. The flavor of the cordial known as *parfait amour* is a mixture of vanilla and rose.

CHEMICAL COMPOSITION. **Rose Oil.**—The yield varies from 0.02 to 0.05 per cent.

Physical and Chemical Values.—The data on authentic material are confined chiefly to the Bulgarian product. German oil usually is a trifle lower in specific gravity. The tentative limits herewith tabulated are based on figures secured by Parry,¹ Irk,² Schimmel & Co.,³

¹ Chem. and Drug. 1909, **75**, 186.

² Pharm. Zentralh. 1913, **54**, 591.

³ Rep. Oct. 1914/Apr. 1915, p. 40.

Siedler,¹ Kyulyumov and Stefanova,² Chiris,³ Zlataroff,⁴ Poucher,⁵ Parry and Seager,⁶ Glichitch and Naves,⁷ and others.

	Sp. gr. 15° C.	Ref. ind. 25° C.	Opt. rot.	Solid. point	Ester No.	Acetyl No.*	Acid No.	Alco- hols, total†	Aleo- hols, com- bined†	Stea- roptene
			°	° C.				%	%	%
Min.	0.848	1.4520	-5	+11	6.0	198	0.5	64	2	6.2
Max.	0.880	1.4681	-1	+27	18.3	248	4.3	84	5	25.0

* Ester number after acetylation. † Calculated as geraniol.

The values of rose oil from Liguria, Italy, as determined by Rostvesti,⁸ are for the most part within the limits given above, except that the minimum for total alcohols is only 31.09 and the maximum for stearoptene is 39.1 per cent.

Glichitch and Naves⁷ give 153.9 to 196.9 for ester number after formylation.

Karaivanoff⁹ reports limits for Bulgarian oils, made from *R. Damascina*, *R. Damascina* var. *alba*, and a hybrid of *R. gallica* and *R. canina*, conforming in general to those given in the table.

The *U. S. Standards* require 0.4 per cent by volume of otto of roses in rose extract.

Constituents.—The oil is made up of (1) *stearoptene*, consisting chiefly or in part of a crystalline hydrocarbon (C₁₆H₃₄) of the paraffin series which separates on cooling, and (2) the liquid portion, constituting fully three-fourths of the oil, consisting chiefly of the alcohols *geraniol* and *citronellol*, largely uncombined, in widely varying proportion, but geraniol predominating.

Stearoptene has been studied by Hanbury¹⁰ and Flückiger.¹¹ *Geraniol* was isolated by Eckart¹² under the name of *rhodinol* and by

¹ Pharm. Ztg. 1915, 60, 179.

² Rev. agr. inst. rech. agr. Bulgare 1921, 2, 84.

³ Parf. France 1924, 15, 107.

⁴ Parf. mod. 1926, 19, 287.

⁵ Parf. Ess. Oil Rec. 1932, 23, 375.

⁶ Ibid. 1933, 24, 149.

⁷ Parf. France 1934, 12, 6.

⁸ Riv. ital. ess. prof. 1932, 14, 195.

⁹ Drug. Cosmet. Ind. 1938, 42, 580.

¹⁰ Sci. Paper 172.

¹¹ Pharmakognosie, Berlin, 1891, p. 169.

¹² Arch. Pharm. 1891, 229, 355.

Markownikoff and Reformatzki¹ under the name of *roseol*, but Bertram and Gildemeister² established the identity of the three. *Citronellol* likewise when first isolated was considered to be a new substance, the *reuniol* of Hesse,³ a name soon displaced after the investigation of Tiemann and Schmidt.⁴ Other constituents stated to be present are esters of the above alcohols, *phenyl-ethyl alcohol*, *l-linaloöl*, *nonylaldehyde*, and *citral*. Von Soden and Treff⁵ announced the presence of *nerol* (C₁₀H₁₈O), and Elze⁶ found *farnesol* in German oil.

Russian oil from Tiflis, examined by Schimmel & Co.,⁷ contained citronellol 27.53, geraniol, and β -phenyl-ethyl alcohol 41.44, esters 2.79, and terpenes 4.77 per cent.

Glichitch and Naves⁸ report in Bulgarian oils considerably over 40 and Karaivanoff⁸ 35 to 51 per cent of rhodinol (geraniol).

¹ J. prakt. Chem. 1893, II, 48, 293.

² Ibid. 1894, II, 49, 185.

³ Ibid. 1894, II, 50, 472.

⁴ Ber. 1896, 29, 922.

⁵ Ibid. 1904, 37, 1094.

⁶ Chem. Ztg. 1919, 43, 747.

⁷ Rep. Oct. 1914/Apr. 1915, p. 40.

⁸ Loc. cit.

FLOWERS OF THE VIOLET FAMILY

(*Violaceæ*)

VARIOUS species of *Viola* have the characteristic violet odor to a greater or lesser degree.

VIOLET

Viola spp.

Fr. Violette. Sp. Violeta. It. Violetta. Ger. Veilchen.

Sugared whole violets are often mixed with bonbons, contributing more in color and fragrance than in agreeable flavor.

Violet Oil, described in works on essential oils, much diluted, may be used for flavoring, but its high cost is usually prohibitive.

Physical and Chemical Values.—The following are by Von Soden: ¹

	Sp. gr. 15° C.	Opt. rot. 17° C.	Ester No.	Acid No.
Flowers	0.920	104.3	37	10
Leaves	0.909	2.3	85	20

Constituents.—Von Soden ¹ believes that the characteristic odor is due to a member of the ionone group. See Orris.

¹ J. prakt. Chem. 1904, II, 69, 256; 1925, II, 110, 273.

FLOWER BUDS OF THE MYRTLE FAMILY

(*Myrtaceæ*)

A SINGLE species yields the cloves of commerce. To this family also belong allspice and various species yielding table fruits.

CLOVES

Eugenia aromatica Baill. = *E. caryophyllata* Thunb. = *Caryophyllus aromatica* L. = *Jambosa Caryophyllus* (Spreng.) Ndz.

Fr. Girofles. Sp. Clavo. It. Garofano. Ger. Gewürznelken.

The dried flower buds of an evergreen tree are the cloves of commerce. The tree is a native of the Moluccas and probably also of the Philippines. The cloves of Amboina, an island of the Moluccas, are well known in commerce. The tree is grown extensively in various tropical regions such as Zanzibar, Madagascar, Réunion, India, and the West Indies.

Clove fruit (mother cloves or anthophylli) occurs rarely in commerce.

MACROSCOPIC STRUCTURE (Fig. 56).—The *flower buds* (I) are 10 to 15 mm. long and are borne in thrice-branching corymbs, the stems of which, after removal of the buds, constitute the *clove stems* of commerce (III). *Cloves* proper consist of (1) the lower fruit axis or hypanthium (*T*); (2) the consolidated axis and ovary, the latter (*O*) having two locules containing numerous ovules; (3) the calyx lobes or teeth (*L*); (4) the corolla (*Co*) closing over (5) the numerous stamens (*A*) and (6) the central columnar style. When the bud is picked the axis and calyx teeth are red, the corolla whitish, but the whole becomes brown on drying. So rich are cloves in volatile oil that drops exude on pressing with the finger nail.

Clove fruit (II) consists of the expanded receptacle and pericarp, crowned with calyx teeth, containing usually but a single seed with fleshy, folded cotyledons.

MICROSCOPIC STRUCTURE.—Descriptions appear in the treatises on the histology of foods and drugs.

Receptacle.—Fig. 57 shows a cross section through the fruit axis below the ovary. Some of the tissues seen in the powder are shown in Fig. 58. The tissues are: (1) *epicarp* (*epi*) of small cells with thick cuticle (*c*) and slightly raised stoma (*sto*); (2) *volatile oil zone*, the numerous cavities (*ol*), up to 200 μ , occurring in two or three tiers; (3) *outer parenchyma* with rather thick, often wavy walls; (4) *outer bundle zone* consisting of an interrupted row of bicollateral fibrovascular bundles (*fv*), accompanied by strongly developed bast fibers (*f*¹) and crystal fibers with rosettes (*cr*, *cr*¹); (5) *middle parenchyma* varying from thick-walled cells with colenchymatous angles to chains of cells forming a network about large intercellular spaces (*b*), and finally to normal small-celled parenchyma; (6) *inner bundle zone* (*r*) of narrower elements than in the outer zone and few bast fibers (*f*²); and

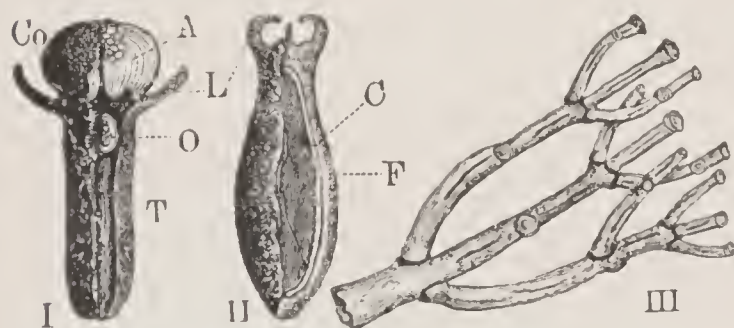


FIG. 56.

FIG. 56.—I Cloves. *T* receptacle; *L* calyx lobes; *Co* corolla; *A* stamens; *O* ovary. $\times 2$. II Clove Fruit. *F* pericarp; *C* cotyledons. $\times 1$. III Clove Stems. $\times 1$. (A.L.W.)

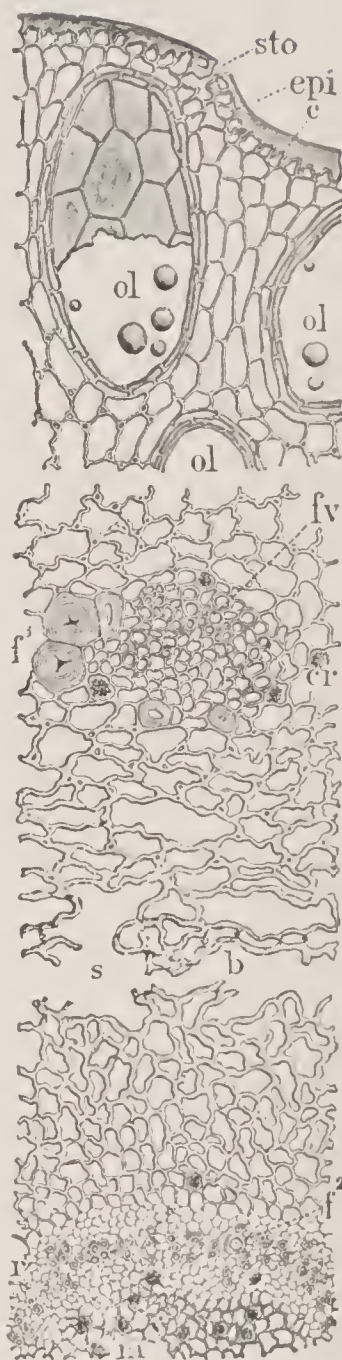


FIG. 57.

FIG. 57.—Cloves. Receptacle (axis) below ovary in cross section. *epi* epiderm with *c* thick cuticle and *sto* stoma; *ol* volatile oil cavities; *fv* bundle of outer ring with *f*¹ bast fibers and *cr* crystal fibers; *s* thick-walled spongy parenchyma; *b* chains of cells; *r* inner bundle ring with *f*² bast fiber; *m* pith with crystal fibers and cells. $\times 160$. (A.L.W.)

(7) *pith* (*m*) of cells larger than in the preceding zone, often with oxalate rosettes.

The *volatile oil cavities*, lined with several rows of thin-walled, flattened secretion cells, are the seat of the only valuable constituent—oil of cloves. These cavities are not distinguishable from those in allspice or those in the pericarp and cotyledons of the rose apple (which see) and other myrtaceous fruits.

The cells in the chains, as shown at *b*, have beaded partitions,

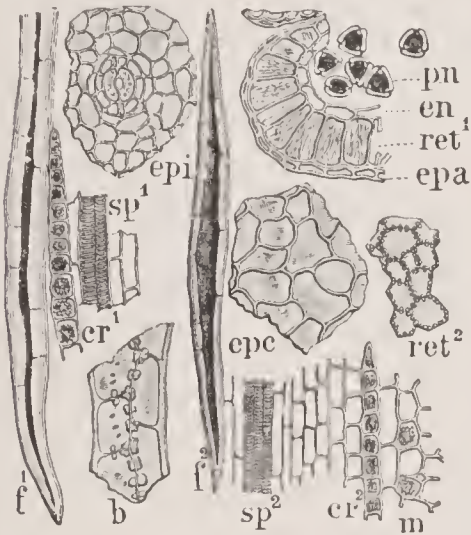


FIG. 58.

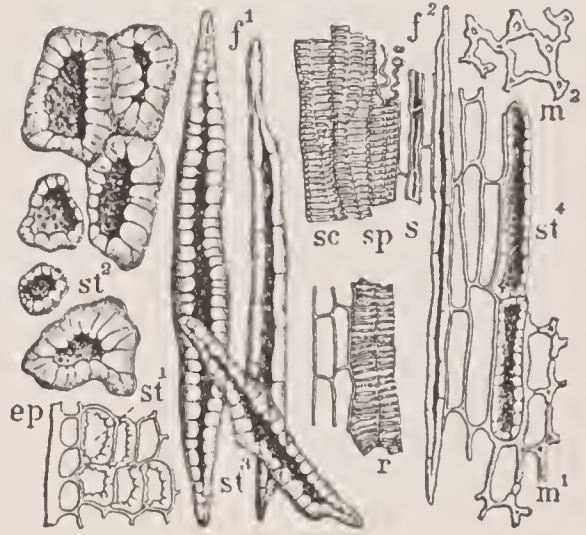


FIG. 59.

FIG. 58.—Cloves. Receptacle in surface view: *epi* epidermis; *f*¹ bast fiber, *cr*¹ crystal fiber, and *sp*¹ spiral vessels of outer bundle ring; *b* chain cells of spongy parenchyma; *f*² bast fiber, *sp*² spiral vessels, and *cr*² crystal fiber of inner bundle ring; *m* pith with crystal cells; oil cavities not shown. *epc* epidermis of corolla. Anther in cross section: *epa* outer epidermis, *ret*¹ reticulated cells, *en* inner epidermis; *ret*² reticulated cells in surface view; *pn* pollen grains. $\times 160$. (A.L.W.)

FIG. 59.—Clove Stems. *ep* epidermis and *st*¹ hypodermal stone cells in cross section; *st*², *st*³ stone cells, and *f*¹ bast fiber outside of bundle ring; *st*⁴ stone cells and *f*² bast fiber inside of bundle ring; *r* reticulated cells; *sc* scleriform vessels; *sp* spiral vessels; *s* sieve tube; *m*¹ pith cells in longitudinal, *m*² in cross section. $\times 160$. (A.L.W.)

while those at *s* are moderately thick-walled throughout. Similar chains about intercellular spaces occur in an exaggerated form in the macopa. Chains are present in the rose apple, but not about intercellular spaces, the meshes being filled with larger and thinner-walled cells.

Receptacle and Ovary.—The consolidated tissue flanking the ovary agrees with that beneath the ovary, as described above, up to the chains of cells in the middle parenchyma. The central bundle zone, together with some of the parenchyma immediately enclosing it, and

the pith are extended into the partition between the two locules of the ovary.

Calyx.—This also agrees in general structure with that of the outer receptacle. *Volatile oil cavities* occur beneath both epiderms.

Corolla.—Both the *outer* and *inner epiderms* (Fig. 58, *epc*) are about the same in structure. Through these tissues may be seen *volatile oil cavities* and *bundle elements*.

Stamens.—The *filaments* consist of elongated cells, many with crystal rosettes, and volatile oil cavities about a central bundle zone. Cross sections of the *anthers* (Fig. 58) show the outer epiderm (*epa*), reticulated cells (*ret*¹), and the inner epiderm (*en*). In surface mounts the reticulated cells (*ret*²) are interesting. The *pollen grains* (*pn*) are triangular.

Clove Stems (Fig. 59).—From without inward the tissues may be classified into six groups: (1) *epiderm* (*ep*), much as in cloves; (2) *hypoderm* of stone cells (*st*¹), thickened in the inner half and arranged in corklike radial rows; (3) zone of *volatile oil cavities* as in cloves; (4) *outer parenchyma* with large isodiametric and elongated stone cells (*st*², *st*³); (5) *bundle zone* flanked with broad bast fibers (*f*¹) on the outer side and narrow bast fibers (*f*²) and rodlike stone cells (*st*⁴) on the inner side of the bicollateral bundles; and (6) *pith* (*m*¹, *m*²) of thick-walled porous cells, with triangular intercellular spaces, arranged in longitudinal rows.

The bast fibers, also the scalariform (*sc*) and spiral (*sp*) vessels, are more woody than in cloves. Transitions from vessels to reticulated cells (*r*) are present.

Clove Fruit or Mother Cloves.—During ripening the elements of the receptacle and ovary become more strongly developed, the *bundle elements* increase in size, and the *bast fibers* become more irregular, approaching stone cells in structure.

The *spermoderm* is so feebly developed as usually to escape notice, but the starch of the cotyledon is conspicuous. The *starch grains* are pear-shaped, club-shaped, or ovate, the narrower end being rounded-truncated. They range up to 40 μ long and often have a distinct hilum in the broad end. Distinct crosses appear on polarization. Starch of the same character occurs in seeds of rose apple and other *Eugenias*.

CHIEF STRUCTURAL CHARACTERS.—Cavities containing the valuable constituent, oil of cloves, in form and structure like those in allspice and succulent myrtaceous fruits.

MICROSCOPY OF GROUND CLOVES.—Identification of the numerous elements of ground cloves requires careful treatment and

patient search. Usually it is sufficient to note the broad bast fibers and the absence of true stone cells, the latter being indicative of ground clove stems, cocoanut shells, or other woody material. Starch is absent in cloves but is the characteristic element of clove fruit. It is pear-shaped to ovate, up to 40 μ long, with hilum in the broad end.

CHEMICAL COMPOSITION.—The analyses of whole cloves and clove stems in the table on p. 296 were made by practically the same methods. The analysts were Richardson,¹ McGill,² Winton, Ogden, and Mitchell,³ and Hodgson.⁴

Winton, Ogden, and Mitchell found 13.99 to 15.92, average **15.01**, and Hodgson 11.55 to 14.90, average **12.79**, per cent of alcohol extract in cloves.

Reich⁵ by methods of his own device determined the volatile oil and eugenol in the volatile oil with the following average results respectively: Amboyna cloves, 4 samples, 21.6, 80.2; Zanzibar cloves, 10 samples, 19.2, 84.2; mother cloves, 4 samples, 2.9 to 9.2, 85; and clove stems, 3 samples, 6.4, 84 per cent. The volatile oil was separated by distillation with steam and extraction by pentane from the distillate after saturation with salt; the eugenol was determined in the volatile oil by treatment with sodium hydroxide, shaking with low-boiling-point petroleum ether, decomposition of the sodium eugenol compound with sulphuric acid, and extraction with pentane.

The *U. S. Standards* require that cloves contain not more than 5 per cent of clove stems, 10 per cent of fiber, 7 per cent of total ash, nor 0.5 per cent of sand, and not less than 15 per cent of volatile ether extract nor 12 per cent of quercitannic acid (calculated from the total oxygen absorbed by the aqueous extract).

Fixed Oil.—This consists of a complex mixture of fatty oil, resins, and other substances including caryophyllin.

Caryophyllin, $C_{20}H_{32}O_2$ or $C_{40}H_{64}O_4$.—The second formula is by Hjelt.⁶ This substance, described by Lodibert,⁷ by Bonastre,⁸ and even earlier, so it is stated, by Baget, is prepared from cloves, after removal of the volatile oil with cold alcohol, by extraction with ether and crystallization. It forms colorless, odorless needles soluble in

¹ U. S. Dept. Agr., Div. Chem. 1887, Bul. **13**, II, 222.

² Canada Lab. Int. Rev. Bul. **73**.

³ Connecticut Agr. Exp. Sta. Rep. 1898, p. 184; 1899, p. 100.

⁴ Am. J. Pharm. 1909, **81**, 6.

⁵ Z. Unters. Nahr-Genussm. 1909, **18**, 401.

⁶ Ber. 1880, **13**, 800.

⁷ J. Pharm. 1825, **11**, 101.

⁸ Ibid. 1825, **11**, 103.

COMPOSITION OF CLOVES AND CLOVE STEMS

	Water	Pro- tein	Oil, fixed	Oil, vola- tile*	Pure starch †	Starch equiv. ‡	Fiber	Crude tan- nin§	Ash, total	Ash, sol- uble	Sand
	%	%	%	%	%	%	%	%	%	%	%
<i>Cloves:</i>											
Richardson											
Min.	2.90	4.73	7.12	10.23	6.18	11.70	5.25
Max.	10.67	7.00	10.24	18.89	9.75	22.13	13.05
Aver. (7)	6.85	5.88	9.51	15.63	8.16	18.30	7.78
McGill											
Penang											
Min.	5.0	9.5	14.8
Max.	7.4	12.0	17.2
Aver. (8)	6.2	10.8	16.2
Amboyna											
Min.	5.5	8.2	18.0
Max.	6.7	10.0	19.2
Aver. (8)	6.1	9.0	18.5
Zanzibar											
Min.	4.1	8.0	12.1
Max.	6.7	10.7	18.3
Aver. (13)	5.7	9.6	16.0
W. O. and M.											
Penang											
Min.	7.81	6.31	5.12	17.99	2.25	8.91	7.85	18.38	5.28	3.25	0.00
Max.	8.16	7.06	6.61	20.04	2.70	9.41	8.74	18.90	5.44	3.48	0.05
Aver. (3)	7.96	6.60	5.99	19.25	2.51	9.16	8.18	18.64	5.34	3.34	0.03
Amboyna											
Min.	7.36	5.94	6.39	20.42	2.59	8.19	7.06	16.25	6.16	3.56	0.02
Max.	8.26	6.00	6.67	20.53	3.15	8.87	8.11	16.90	6.22	3.72	0.08
Aver. (3)	7.89	5.96	6.56	20.47	2.80	8.43	7.71	16.64	6.18	3.62	0.04
Zanzibar											
Min.	7.03	5.88	6.24	17.82	2.08	9.18	8.24	18.28	5.96	3.61	0.08
Max.	7.93	6.25	6.59	18.32	3.15	9.63	9.02	20.54	6.22	3.75	0.13
Aver. (3)	7.62	6.02	6.45	18.00	2.73	9.44	8.62	19.44	6.07	3.68	0.10
Bencoolen (1) ...	6.73	6.12	5.14	20.09	2.62	9.60	6.00	3.80	0.03
All var.	7.71	6.19	6.22	19.32	2.68	8.99	8.31	18.19	5.88	3.57	0.06
Hodgson											
Min.	7.02	5.69	6.24	17.82	9.50	17.13	4.20
Max.	8.26	5.94	6.39	20.53	10.55	20.54	6.94
Aver. (12)	7.95	5.81	6.29	18.90	10.00	18.19	5.45
<i>Clove Stems:</i>											
Richardson (1) ...	10.18	5.78	4.03	4.40	13.58	23.24	6.96
W. O. and M. (2) .	8.74	5.88	3.83	5.00	2.17	14.13	18.71	18.79	7.99	4.26	0.60

* Volatile ether extract. † Diastase method; no true starch present. ‡ Reducing matter, after washing with 10% alcohol and direct inversion of residue, calculated as starch. § Tannin equivalent to oxygen absorbed.

ether and warm alcohol. Mylius¹ states that the crystals sublime at 285° C. and on oxidation with fuming nitric acid pass into caryophyll-ic acid (C₂₀H₃₂O₆).

¹ Ber. 1873, 6, 1053.

Eugenin.—Bonastre¹ secured from the aqueous portion of the distillate, after separation of the volatile oil, crystals of a substance which, according to Dumas, has the same empirical formula as eugenol. Martius² estimated the content at 1 per cent, but Flückiger³ was unable to separate any of the substance.

Volatile Oil.—Oil of cloves of the best grade is made from whole cloves by steam distillation. Clove stems yield an inferior grade, although measured by the eugenol content it may be of good strength. Zäch,⁴ by Von Fellenberg's chromic acid oxidation method, obtained 16 to 20 per cent from whole cloves.

Physical and Chemical Values.—The commercial product of known purity varies within the following limits, the hydrogen number, being by Albright,⁵ obtained by his method.

	Sp. gr. 15° C.	Ref. ind. 25° C.	Opt. rot.	Boiling point	Hydrogen No.	Eugenol	Sol. 70% alcohol
			°	°C.		%	vols.
Min. . .	1.043	1.528	−1.2	250	114.0	80	1
Max. . .	1.070	1.537	0.0	260	114.6	95	2

Schimmel & Co.⁶ have published the following data on the oil from different parts of the tree and from young (8 to 9 years) and old (45 to 60 years) trees:

	Yield	Sp. gr. 15° C.	Opt. rot.	Eugenol
	%		°	%
Cloves:				
Young tree	17.8	1.056	−0.4	89
Old tree, buds immature	19.2	1.064	−0.5	88
" " buds mature	18.8	1.049	−0.5	84
" " full flower	17.4	1.050	−0.6	88
" " mostly fruit	6.5	1.056	−0.5	90
Clove stems	6.3	1.050	−0.7	89

¹ J. Pharm. 1835, 20, 565.

² Jahresb. Pharm. 1859, p. 168.

³ Pharmakognosie, Berlin, 1891, p. 800.

⁴ Mitt. Lebensm. Hyg. 1932, 28, 156.

⁵ J. Am. Chem. Soc. 1914, 36, 2188.

⁶ Rep. Oct. 1915, 46.

The *U. S. Standards* require not less than 2 per cent of oil of cloves in clove extract.

From clove stems Gadre ¹ obtained a yield of 4.5 per cent of volatile oil with the following values: specific gravity 34° to 37° C. 1.0522 to 1.0548; refractive index 1.5345; soluble in 0.5 volume of 80 per cent alcohol; total eugenol (Umney) 93.09, (Thom) 83.53, free eugenol (Varley and Bolsing) 69.86 per cent.

The volatile oil from clove stems and clove leaves, both from Combani in Mayotta, examined at the laboratory of A. Chiris ² gave respectively: specific gravity at 15° C. 1.053, 1.045; refractive index at 20° C. 1.5364, 1.5348; saponification number 15.4, 12.6; eugenol (3 per cent soda) 88 to 89, 85 per cent; and solubility in 70 per cent alcohol 1.2 volumes, 1 volume.

From the above results it appears that the oils from the buds, flowers, fruit, stem, and leaves are nearly the same in values and eugenol content.

Constituents.—In addition to *eugenol*, the chief constituent, oil of cloves contains a considerable amount of the sesquiterpenes α - and β -*caryophyllene*, first isolated by Church ³ and further studied by Wallach ⁴; also *acetoeugenol* (Erdmann ⁵ 2 to 3 per cent; Spurge ⁶ 7 to 17 per cent; further studied by Herold ⁷); *salicylic acid* (Schenck ⁸); and *vanillin* (Jorissen and Haüs ⁹). Schimmel & Co. ¹⁰ in various reports give *methyl-n-amylketone* ($C_5H_{11}CO \cdot CH_3$), *methyl heptylketone* ($C_7H_{15}CO \cdot CH_3$), *methyl benzoate*, *acetic acid*, *methyl alcohol*, and *furfural*, and Masson ¹¹ *methyl-n-amyl carbinol*, *furfuryl alcohol*, *methyl-n-heptyl carbinol*, *benzyl alcohol*, α -*methyl furfural*, and *dimethyl furfural*.

Eugenol or paraoxy-metamethoxy-allyl benzene, $C_{10}H_{12}O_2$ or $CH_3O \cdot C_6H_3(CH_2 \cdot CH : CH_2)OH$. This phenol is not only the chief flavoring principle of cloves and allspice but also the initial substance in the manufacture of synthetic vanillin. When pure it is a colorless

¹ Perf. Ess. Oil Rec. 1921, **12**, 115.

² Parf. France 1924, **16**, 152.

³ J. Chem. Soc. 1875, **28**, 113.

⁴ Ann. 1892, **271**, 287.

⁵ J. prakt. Chem. 1897, II, **56**, 143.

⁶ Pharm. J. 1903, **70**, 701, 757.

⁷ Riechstoff Ind. 1930, **5**, 100.

⁸ Ann. 1863, **125**, 14.

⁹ Rev. intern. sci. pop. fals. denr. aliment. 1890, **4**, 32.

¹⁰ Rep. Oct. 1896, 27; Apr. 1897, 45; Apr. 1902, 24; Apr. 1903, 25, 26.

¹¹ Compt. rend. 1909, **149**, 630, 795.

liquid, but soon darkens owing to oxidation. Its specific gravity at 15° C. is 1.0696; its boiling point is variously given from 247 to 255° C. Albright¹ found the hydrogen number to be 134.4. It does not polarize. In alcoholic solution it gives a blue coloration with ferric chloride, changing slowly to green and yellow. It is insoluble in water, but is soluble in alcohol (2 volumes of 70 per cent), dilute alkalies, and glacial acetic acid. Alcoholic potassium hydroxide with the aid of heat converts eugenol into isoeugenol, $\text{CH}_3\text{O} \cdot \text{C}_6\text{H}_3(\text{CH} : \text{CH} \cdot \text{CH}_3)\text{OH}$, by changing the allyl group into the glyceryl group. The solubility of eugenol in a solution of caustic alkali is utilized in its manufacture from oil of cloves. The terpenes which remain insoluble after this treatment are separated as an oily layer and the eugenol is then liberated by dilute acid.

Caryophyllene, $\text{C}_{15}\text{H}_{24}$, not to be confused with caryophyllin, is a sesquiterpene occurring in cassia and cinnamon oils, as well as in different parts of the clove tree. When pure it is a colorless liquid. Its specific gravity at 15° C. is 0.908, its boiling point about 259° C., and its optical rotation -9° . Clovene, which does not appear to occur in oil of cloves, is an isomer of caryophyllene, obtained by splitting off the hydroxyl group from caryophyllene alcohol ($\text{C}_{15}\text{H}_{24}\text{OH}$).

Semmler and Mayer,² after extensive research, conclude that natural or crude caryophyllene consists of (1) inactive α -caryophyllene, probably the same as humulene, (2) limonene caryophyllene, and (3) terpinolene caryophyllene. Probable formulas are given.

Acetoeugenol, $\text{C}_{12}\text{H}_{14}\text{O}_3$ or $\text{CH}_3\text{O} \cdot \text{C}_6\text{H}_3(\text{CH}_2 \cdot \text{CH} : \text{CH}_2) \cdot \text{OCOCH}_3$, is a crystalline substance melting at 30° C. and soluble in alcohol and ether.

Pentosans.—In dry matter 7.48 per cent. See also Introduction to Part III (Hanus and Bien).

Tannin.—Ellis of Toronto suggested to Richardson³ that the tannin content might be of diagnostic value, but apparently did not himself publish any data. Richardson concluded that the tannin equivalent to the total oxygen absorbed from potassium permanganate solution, after removal of ether-soluble matter, was of quite as much value as the percentage of pure tannin, hence his abridgment of the Löwenthal method which has been adopted by American analysts whose results appear herewith.

¹ J. Am. Chem. Soc. 1914, **36**, 2188.

² Ber. 1911, **44**, 3657.

³ U. S. Dept. Agr., Div. Chem. 1887, Bul. **13**, II, 226.

Mineral Constituents.—An analysis given by König,¹ but without stating the analyst, shows:

K ₂ O	Na ₂ O	CaO	MgO	Fe ₂ O ₃	P ₂ O ₅	SO ₃	SiO ₂	Cl
% 62.86	% 0.93	% 0.50	% 1.11	% trace	% 28.40	% 1.65	% 1.00	% trace

¹ Chem. mensch. Nahr.-Genussm., Berlin, 1920, 2, 878.

FRUIT AND SEED SPICES

NUMEROUS fruits and seeds are used for seasoning and flavoring. In some instances, such as the rinds of citrus fruits, only a part of the fruit is valuable for these purposes.

FRUITS OF THE PINE FAMILY

(*Pinaceæ*)

THE species described below is not used directly as a food but on distillation yields a valuable flavor.

JUNIPER BERRY

Juniperus communis L.

Fr. Baies de genièvre. Sp. Bayas de enebro. It. Coccola di ginepro.
Ger. Wacholderbeere.

In the manufacture of gin, juniper berries are distilled with the mash or else juniper oil is added to raw spirits.

MICROSCOPIC STRUCTURE.—See works on pharmacognosy.

CHEMICAL COMPOSITION. Volatile Oil.—The yield of oil varies from 1 to 2 per cent. Other parts of the tree yield an oil of different composition.

Physical and Chemical Values.—Umney¹ notes that the specific gravity of the oil materially increases on aging.

The following limits are based on reliable data:

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Ester No.	Acetyl No.*	Acid No.	Sol. 90% alcohol
			°				vols.
Min. . .	0.860	1.472	−18	1	19	5
Max. . .	0.885	1.488	+ 1	21	69	3	10

* Ester number after acetylation.

¹ Perf. Ess. Oil Rec. 1913, 4, 402.

The physical values for Hungarian oil, as determined by Fölsch¹ and Janiesek² are within the above limits.

Constituents.—As brought out by Wallach,³ *α-pinene* is the chief constituent. Schimmel & Co.⁴ have reported *cadinene*, *terpineol*,⁵ the only oxygenated constituent occurring in considerable amount, *camphene* and *isoborneol*,⁶ and so-called *juniper camphor*⁷ which separates as crystals from the last run of the still. Rodie⁸ found traces of *camphene* and *phellandrene*. Palazzo and Alinari⁹ have secured evidence of the presence of a hydrocarbon of lower specific gravity than pinene.

Indian seed, as distilled by Simonsen,¹⁰ yielded 0.2 per cent of oil resembling savin oil, containing about 50 per cent of *d-sabinene* but no *α-pinene*.

Pentosans.—In dry matter 8.48 per cent. See also Introduction to Part III (Hanus and Bien).

¹ Riechstoff Ind. 1928, 3.

² Ibid. p. 211.

³ Ann. 1885, 227, 277.

⁴ Rep. Apr. 1890, 43.

⁵ Ibid. Oct. 1909, 71.

⁶ Ibid. 1910, 72.

⁷ Ibid. Oct. 1895, 46.

⁸ Rev. gén. chim. 1906, 9, 444; 1907, 10, 18.

⁹ Atti cong. naz. chim. pura appl. 1923, 309.

¹⁰ Ind. Forest Rec. 1924, 11, 6.

FRUITS OF THE GINGER FAMILY

(*Zingiberaceæ*)

PLANTS of this family not only have pungent principles in their subterranean parts (e.g., ginger, turmeric) but also in their seeds.

Malabar, short, or true cardamom (*Elettaria Cardamomum* White et Maton) is the most important of the group. Among others of lesser importance are Ceylon, wild, or long cardamom, a large variety of *E. Cardamomum*, Siam or round cardamom (*Amomum Cardamomum* L.), Java cardamom (*A. maximum* Roxb.), Madagascar cardamom (*A. angustifolium* Sonn.), Bengal cardamom (*A. subulatum* Roxb.), wild cardamom (*A. xanthioides* Wall.), Chinese round cardamom (*A. globosum* Lour.), nutmeg cardamom (*A. Korarima* Pereira), grains of paradise (*A. Mellgueta* Roscoe), and probably other species.

COMPARATIVE MICROSCOPIC STRUCTURE.—Schad¹ describes the comparative histology of the group and gives an analytical key based on the structure of the seed.

CARDAMOM

Elettaria Cardamomum White et Maton

Fr. Cardamome. Sp. Cardamomo. It. Cardamonio.

Ger. Kardamomen.

The fruit of only one variety, the Malabar, Ceylon-Malabar, or short cardamom, is commonly recognized in the spice trade and by the United States Pharmacopœia. As a domestic spice it is little known except as an ingredient of mixed spices, but it is one of the numerous flavors employed by professional cooks, bakers, and cordial manufacturers. Long Ceylon cardamom is inferior.

MACROSCOPIC STRUCTURE (Fig. 60).—Calyx and corolla are tubular, each with three lobes. The ovary is inferior. The fruit (I, II) is 1 to 3 cm. long and has a dry, leathery, cream-colored pericarp. In cross section (III) the fruit is trefoil-shaped and shows three

¹ Inaug. Dis. Bern, 1897.

locules formed by papery partitions, each with a double row of anatropous seeds. The *seeds* (IV, V) are brown with a silvery sheen due to the aril. Several wrinkles run transversely around the seed, interrupted by the depression over the raphe (*R*) on the ventral side which ends toward the apex at the chalaza (*C*). At the base are the hilum (*H*) and the micropyle.

A cross section of the seed (VI) shows that it consists largely of perisperm (*N*) in which is a small endosperm (*E*) and in the endosperm a minute embryo (*Em*).

MICROSCOPIC STRUCTURE.—Cardamom is described by Berg in his Atlas and by later authors. Schad¹ has studied its development.

Pericarp.—The *epicarp* is of polygonal cells, the *endocarp* of elongated cells. Spiral vessels, up to 50 μ , and bast fibers occur in the fibrovascular bundles of the *mesocarp*.



FIG. 60.

FIG. 60.—Cardamom. I and II fruit. $\times 1$. III fruit in cross section showing seeds. $\times 1$. IV ventral and V dorsal side of seed: *H* hilum; *R* raphe; *C* chalaza. $\times 2$. VI seed in cross section: *A* aril; *S* spermoderm; *N* perisperm; *E* endosperm; *Em* embryo. $\times 8$. (A.L.W.)

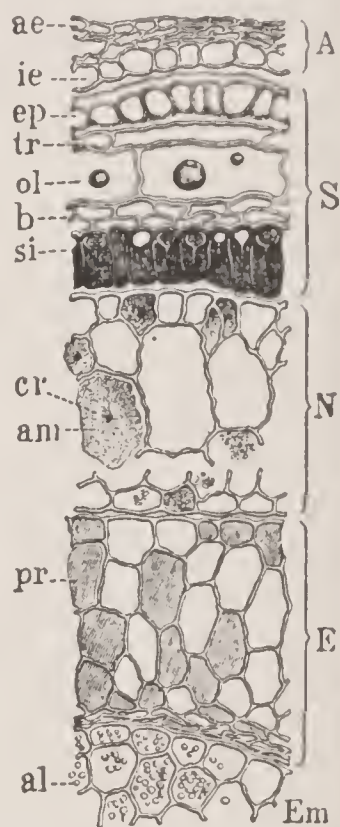


FIG. 61.

FIG. 61.—Cardamom. Seed in cross section. *A* aril: *ae* outer and *ie* inner epiderm. *S* spermoderm: *ep* outer epiderm; *tr* cross cells; *ol* oleoresin layer; *b* beaded parenchyma; *si* palisade cells with siliceous bodies. *N* perisperm: *am* starch; *cr* oxalate crystal. *E* endosperm: *pr* protein masses. *Em* embryo: *al* aleurone grains. $\times 160$. (A.L.W.)

Aril (Fig. 61, *A*; Fig. 62).—Much-elongated cells form the *outer* (*ae*) and *inner* (*ie*) *epiderm*. Oxalate crystals (*ox*) occur in considerable numbers.

Spermoderm (Fig. 61, *S*; Fig. 62).—Five well-marked layers are evident in cross section and surface mounts: (1) *outer epiderm* (*ep*)

¹ Loc. cit.

of elongated cells; (2) *subepiderm* (*tr*) of cross cells; (3) *oleoresin layer* (*ol*) of cross cells, larger and higher than those of the subepiderm, containing oil drops; (4) *beaded parenchyma* (*b*) of small cells with yellow or brown contents; and (5) *palisade cells* (*si*) with greatly thickened, dark brown walls and a siliceous body in the outer end of each cell.

Ceylon cardamom with fruit up to 4 cm. long, produced by a variety of the same species as Malabar cardamom, has in surface view thicker epidermal walls (double walls $6\ \mu$).

The *palisade cells* are of special interest. In the inner part the lumen is reduced to a mere line, whereas the cavity in the extreme outer end is completely filled by a siliceous body much like that occurring in the stigmata of the cocoanut (which see).

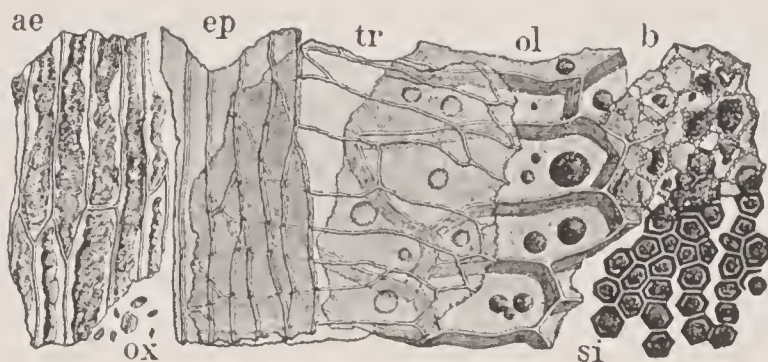


FIG. 62.—Cardamom. Elements in surface view. Aril: *ae* outer epiderm; *ox* oxalate crystals. Spermoderm: *ep* outer epiderm; *tr* cross cells; *ol* oleoresin layer; *b* beaded parenchyma; *si* palisade cells with siliceous bodies. $\times 160$. (A.L.W.)

Perisperm (Fig. 61, *N*).—Throughout, the cells are packed with a mass of minute starch grains, mostly less than $3\ \mu$, in the center of which is a group of oxalate crystals.

The **Endosperm** (Fig. 61, *E*) contains a horny mass rich in protein matter staining bright yellow with iodine in potassium iodide.

Embryo (Fig. 61, *Em*).—Aleurone grains (*al*) and fat are the visible contents.

CHIEF STRUCTURAL CHARACTERS.—Fruit three-celled; pericarp leathery. Seeds numerous, wrinkled. Arils thin.

Spermoderm with thick-walled palisade layer containing siliceous bodies. Perisperm with minute starch grains. Endosperm with horny protein masses. Embryo with aleurone grains.

CHEMICAL COMPOSITION.—Arnst and Hart¹ analyzed separately the kernels and hulls of Malabar and Ceylon (wild) cardamoms. Their method for the determination of volatile oil is essentially the same as described by Richardson,² except that the ground spice is first dried at 100° C. which if long continued entails loss of sufficient volatile oil to vitiate the result.

COMPOSITION OF CARDAMOM (ARNST AND HART)

	In whole	Water	Protein	Oil, fixed	Oil, volatile*	N-f. ext.	Sugar	Starch	Fiber	Ash
	%	%	%	%	%	%	%	%	%	%
Kernel:										
Malabar.....	57	11.25	14.77	1.73	3.83	31.13	0.64	21.73	16.69	10.60
Ceylon.....	65	12.25	12.96	2.05	2.85	48.13	0.45	40.53	14.37	7.39
Hulls:										
Malabar.....	43	9.52	7.64	2.56	0.13	38.27	1.16	20.80	29.99	11.89
Ceylon.....	35	9.15	10.12	3.07	0.07	36.39	0.84	18.66	28.67	12.53

* Volatile ether extract.

The *U. S. Standards* require that the seed contain not more than 8 per cent of total ash nor more than 3 per cent of sand.

Volatile Oil.—The essential oil distilled from short cardamom, including Malabar, Mysore, and cultivated (not wild) Ceylon, is commonly recognized as the standard. That from long, wild, or Ceylon and from Siam cardamoms is inferior. By the Von Fellenberg chromic acid oxidation method, Zäch³ obtained 2 to 10 per cent. Clevenger⁴ has demonstrated that the loss of volatile oil from shelled cardamom seed reaches about 30 per cent in eight months, but is relatively slight in the undecorticated seed.

Physical and Chemical Values.—The following limits of values are based on results by Schimmel & Co.,⁵ Beringer,⁶ Parry,⁷ and Sage,⁸ as well as earlier authors:

¹ Z. angew. Chem. 1893, **6**, 136.

² U. S. Dept. Agr., Div. Chem. 1887, Bul. **13**, II.

³ Mitt. Lebensm. Hyg. 1932, **23**, 156.

⁴ J. Ass. Off. Agr. Chem. 1934, **17**, 283.

⁵ Rep. Apr. 1910, 29.

⁶ Am. J. Pharm. 1910, **82**, 167.

⁷ Perf. Ess. Oil Rec. 1918, **9**, 31.

⁸ Ibid. 1924, **15**, 150.

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Ester No.	Acid No.	Sol. 70% alcohol
Short (Malabar)			°			vols.
Min.....	0.923	1.4600	+21	94	2.0
Max.....	0.947	1.4700	+46	150	4.0	5.0
Long (Ceylon)						
Min.....	0.895	1.4740	+12	1.0
Max.....	0.909	1.4775	+17	12	1.1	2.5
Round (Siam).....	0.905*	+38

* At 42°.

Parry found that the oils from Bengal cardamoms (*Amomum aromaticum*), Cameroon cardamoms, and Korarima cardamoms (*A. korarima*) are levorotatory. The last named has a nutmeg odor.

Constituents.—Schimmel & Co.¹ give *terpinyl acetate*, *d-α-terpineol*, and *cineol* as the chief constituents of true cardamoms. Terpenes have not been isolated. In long or Ceylon cardamoms, Weber ² found *terpineol* and *terpinene*. Wallach ³ isolated the terpene *sabinene* yielding dichlorhydrate. In Siam cardamoms, according to Schimmel & Co., *d-borneol* and *d-camphor*, both solids, are present.

Carbohydrates. *Starch* and *Sugar*.—See table above.

Pentosans.—Hanus and Bien ⁴ found in Ceylon seed 2.37 and in Malabar seed 2.62 per cent, dry basis. See Introduction to Part III.

Mineral Constituents.—The composition of the ash of whole cardamoms by Yardley ⁵ follows:

Ash	K ₂ O	Na ₂ O	CaO	MgO	Fe ₂ O ₃	Al ₂ O ₃	P ₂ O ₅	SO ₃	SiO ₂	Cl	CO ₂ etc.
%	%	%	%	%	%	%	%	%	%	%	%
4.19	20.43	10.42	13.33	4.52	0.51	1.53	6.00	12.66	24.81	2.54	4.40

¹ Rep. Oct. 1897, 9.

² Ann. 1887, 238, 98.

³ Ibid. 1906, 350, 168.

⁴ Z. Unters. Nahr.-Genussm. 1906, 12, 395.

⁵ Chem. News 1899, 79, 122.

FRUITS OF THE ORCHID FAMILY

(*Orchidaceæ*)

ONLY one genus, *Vanilla*, is here described.

VANILLA

Vanilla planifolia Andrew

Fr. Vanille. Sp. Vainilla. It. Vainiglia. Ger. Vanille.

Of the flavoring materials used for sweetened foods vanilla is the most highly esteemed. Alone it is indescribably delicate; with chocolate it forms a perfect combination.

The plant is a vine with aerial roots which find their way into the soil. It is a native of Mexico, where the finest grade of vanilla bean is still produced, and is cultivated in other tropical regions. Arranged approximately in the order of their commercial value the common grades on the market are Mexican, Bourbon (including the products of Réunion, Seychelles, and Madagascar), South American, Java, Ceylon, Fiji, and Tahiti, the last in the list being of recognized inferior flavor.

The *vanilla bean* is picked while still green and is subjected to a sweating process, the care with which this is carried out determining to a large degree the perfection of the flavor.

Vanilla is most commonly used in the United States in the form of *vanilla extract* so prepared, according to the *U. S. Standards*, with dilute alcohol, and usually sugar, that 100 cc. of the finished product contains the soluble matter of 1 gram of vanilla bean. Such a standard does not, however, recognize the great variation in the beans both in moisture and vanillin content.

Ground vanilla beans are used extensively abroad and to some extent by American cooks.

Synthetic vanillin takes the place of true vanilla in the manufacture of cheap flavors, both liquid (vanillin solution) and solid (vanillin sugar). A solution containing the same percentage of vanillin as true vanilla extract costs hardly a twentieth as much yet the genuine

product holds its own with the discriminating consumer as the vanillin flavor is modified and perfected by certain minor constituents which have not all been imitated.

Commercial vanillin, itself a substitute, at one time was often substituted in part by acetanilide, a substance of no flavoring value. Winton and co-workers reported a number of cases where vanilla extract contained acetanilide thus introduced.

Vanirom, the ether of protocatechuic aldehyde, has flavoring strength four times that of vanillin and is being substituted for it in the manufacture of vanillin sugar. Dingemans¹ states that it may be detected in an ether solution by the lemon yellow precipitate formed on adding a saturated solution of hydrazine sulphate followed after a few minutes by fourth normal hydrochloric acid. Vanillin gives an orange-red precipitate.

Coumarin, another substitute often used in conjunction with vanillin, whether derived from the tonka bean (which see) or prepared synthetically, is a ranker flavor.

MACROSCOPIC STRUCTURE.—Three sepals and three petals, both yellow and united with the one-celled ovary, form the perianth of the *flower*. The ovary is one-celled, but has three pairs of parietal placentæ with great numbers of minute ovules. In cross section the narrow, elongated *fruit*—most inappropriately known as a bean—is rounded-triangular. The *seeds* are 0.2 to 0.4 mm. long with a tough black spermoderm and a bulky embryo. Cotyledons and radicle are not well differentiated, and endosperm is lacking.

Commercial vanilla beans (Fig. 63) are longitudinally striate, of a deep chocolate brown color, and oily luster. In 78 samples representing different kinds, grades, and lengths, examined by Winton and Berry,² the length varied from 10 to 23 cm., the average being 16 cm. A few millimeters from the apex there is a constriction and at the end there is a depression. At the base there is a sharp curve. Vanillin crystals often coat the surface of the bean.

MICROSCOPIC STRUCTURE. **Pericarp** (Figs. 64 and 65.)—The *cuticle* (*c*) consists of a thin, uniform outer lamella and a thicker, granular inner lamella. Together these may be thicker or thinner than the wall proper of the epicarp.

Four cellular layers are present: (1) *epicarp* (*e**pi*) of more or less longitudinally elongated, beaded cells, each containing an oxalate crystal, a cell nucleus, and a formless brown matrix, also stomata; (2)

¹ Chem. Weekblad 1930, 27, 694.

² U. S. Dept. Agr., Bur. Chem. 1912, Bul. 152.



FIG. 63.

hypoderm (*hy*) of one or two layers of cells similar to those of the epicarp but often with diagonal pores, also occasional raphides cells; (3) *mesocarp* of ground tissue with cell walls often spirally thickened (*rc*), raphides cells, and fibro-vascular bundles with bast fiber sheath (*f*); and (4) *endocarp* (*end*) of club-shaped hairs secreting oleoresin (*ol*).

Of particular interest are the *reticulated cells* (*rc*) of the hypoderm and mesocarp, the thickenings of which are spirally arranged. Several authors state that these occur only in Mexican beans. Moeller¹ finds them in Central American as well as Mexican beans, while Vogl² states that they are sometimes absent in Mexican beans and

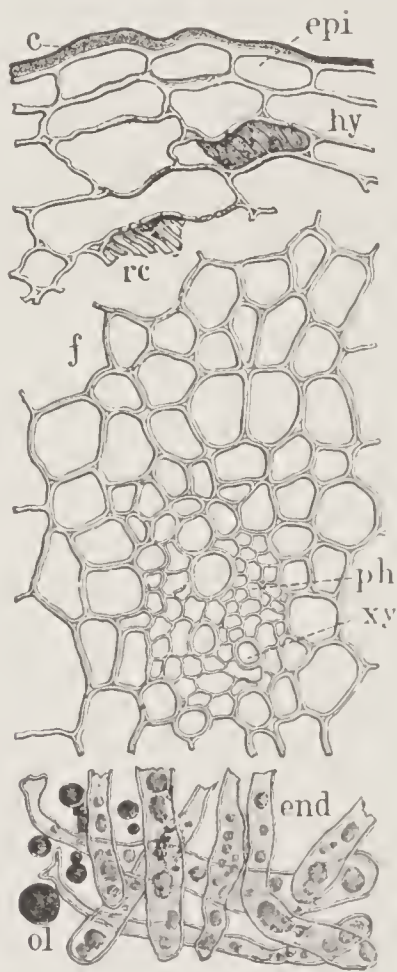


FIG. 64.

FIG. 63.—Vanilla Bean. $\times 1$. (A.L.W.)

FIG. 64.—Vanilla. Pericarp in cross section. *c* cuticle; *e**pi* epicarp; *h**y* hypoderm; *f* bast fibers, *ph* phloem and *xy* xylem of bundle; *end* endocarp; *ol* oleoresin drops. $\times 160$. (A.L.W.)

¹ Mikros. Nahr.-Genussm., Berlin, 2. Aufl. 1905, p. 378.

² Wicht. Nahr.-Genussm., Berlin, 1899, p. 458.

sometimes present in Bourbon beans. The writers find that they furnish no criterion of geographical origin but that their presence indicates full maturity.

Characteristic of the *fibro-vascular bundles* are the bast fibers (*f*) of the sheath with elliptical, not diagonal, pores. Sometimes two bundles are consolidated with a common sheath and a wedge of fibers between the bundles proper.

Hairs form the endocarp between adjoining pairs of placentæ. Between the individual placentæ of each pair peculiar, very narrow,

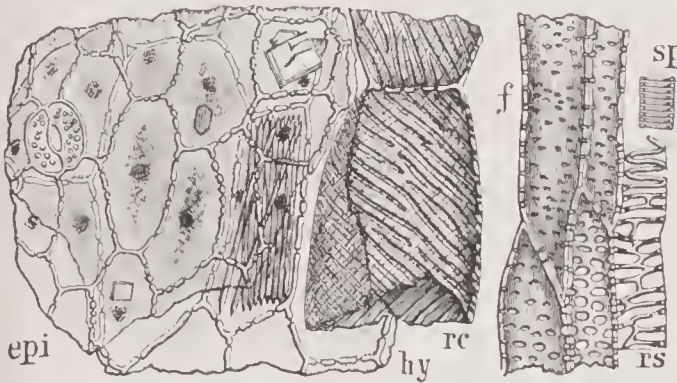


FIG. 65.

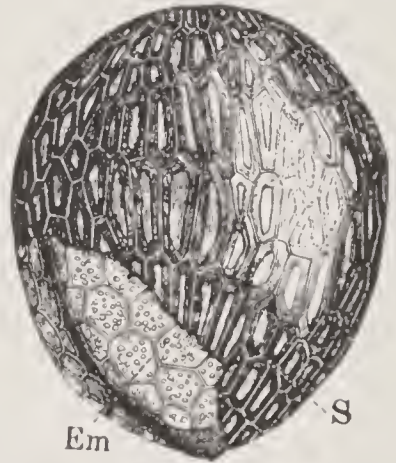


FIG. 66.

FIG. 65.—Vanilla. Pericarp in surface view. *epi* epicarp with prismatic oxalate crystals; *hy* hypoderm with raphides; *rc* spiral-reticulated cells; *f* fibers; *rs* reticulated-spiral vessel; *sp* spiral vessel. $\times 160$. (A.L.W.)

FIG. 66.—Vanilla. Seed in surface view. *S* outer epiderm of spermoderm; *Em* embryo. $\times 160$. (A.L.W.)

longitudinally elongated mucilage cells facilitate the passage of the pollen tubes to the ovules.

Speroderm (Fig. 66, *S*).—Only one layer is ordinarily evident, and the structure of this layer in ripe seeds is evident only after removal of the dark pigment by boiling with sodium hydroxide. The cells are polygonal-elongated with greatly swollen walls. The inner layers are obliterated or obscure.

Embryo (Fig. 66, *Em*).—The polygonal cells contain fat and small aleurone grains, the latter being evident after extraction of the fat.

CHIEF STRUCTURAL CHARACTERS.—Beans elongated, striate, dark. Seeds numerous, minute, black, on three placentæ.

Cuticle with granular inner lamella. Epicarp of elongated cells containing oxalate prisms; hypoderm and mesocarp with spiral-reticulated cells and raphides cells; fibro-vascular bundles collateral,

often double, bast fibers with oval pores. Spermoderm of dark elongated cells with swollen walls.

CHEMICAL COMPOSITION.—Only a few proximate analyses of whole vanilla beans have appeared in the literature, those quoted by König ¹ and Hanausek ² being two analyses by Laube and Aldendorf ³ as follows:

	Water	Protein	Fatty oil	Volatile oil	N-f. ext.	Sugar	Fiber	Ash
	%	%	%	%	%	%	%	%
I.	30.93	2.56	4.68	32.90	9.12	15.27	4.53
II.	25.85	4.87	6.74	0.64	30.50	7.07	19.60	4.73

Vanilla Extract.—Tiemann and Haarmann ⁴ give the following percentages of vanillin occurring in different varieties of vanilla beans: Mexican 1.32 to 1.69, Bourbon 0.75 to 2.90, and Java 1.56 to 2.75 per cent.

Figures obtained by adding the precentages of vanillin found by Winton and Berry in the first and second extracts described below, and calculating to the basis of the beans, are here summarized:

VANILLIN CONTENT OF VANILLA BEANS (WINTON AND BERRY)

	Samples	Min.	Max.	Aver.
		%	%	%
Mexican.....	13	1.8	2.2	2.0
Bourbon.....	16	1.6	2.7	2.1
Seychelles.....	9	1.9	2.5	2.3
Madagascar.....	9	2.0	3.4	2.6
Comores.....	16	1.5	3.2	2.1
So. American.....	3	1.9	2.5	2.3
Ceylon.....	3	2.3	2.7	2.5
Java.....	3	2.5	2.8	2.7
Tahiti.....	2	1.3	1.3	1.3
Vanillons.....	1	0.7	0.7	0.7

¹ Chem. mensch. Nahr.-Genussm., Berlin, 1903, 1, 960.
² Nahr.-Genussm., Kassel, 1884, p. 286.
³ Hannoversche Monatsschr. "Wider die Nahrungsfälscher," 1879, p. 83.
⁴ Ber. 1875, 8, 1115; 1876, 9, 1287.

The table on the following page summarizes the results of Winton and Berry¹ on vanillin, normal lead number, and color values, and of Winton, Albright, and Berry² on acidity, ash, and alkalinity of the ash of extracts prepared in the laboratory by the formula of the 8th revision of the U. S. Pharmacopœia (1907) which differs from that of the last revision of the National Formulary (1926) only in details of manipulation. In the process employed, 100 grams of cut and bruised beans were macerated with 500 cc. of dilute alcohol (650 cc. 95 per cent alcohol and 350 cc. of water) for 12 hours, the liquid was decanted off, and the residue was ground with 200 grams of sugar. The mixture was then transferred to a percolator with fresh portions of the dilute alcohol and the percolation continued until the total extract measured 1 liter.

The vanillin was determined by the Hess and Prescott method,³ slightly modified to permit the determination of normal lead number and color values of the lead filtrate in one portion. The normal lead number—so called because normal lead acetate is used—was determined by the Winton and Lott method,⁴ the color value of the extract and the lead filtrate by measurements in the Lovibond tintometer, and the color insoluble in amyl alcohol by the Marsh test as used by Tolman and Hillyer⁵ for the examination of whisky and further modified by Hiltner for application to vanilla extracts. Color values in all cases are reduced to the basis of the original extract and a 1-inch cell.

The results bring out striking characters of genuine vanilla extract as compared with those of factitious flavoring solutions prepared from synthetic vanillin and caramel color which are characterized by their low lead numbers and also by high percentages of color in the lead filtrate and insoluble in amyl alcohol.

The residues from the preparation of the extracts were soaked for five months in alcohol and these second extracts analyzed for certain constituents. A summary of the results covering all varieties reduced to the basis of the first extract follow: vanillin 0.01 to 0.07, aver. **0.03**; normal lead number 0.03 to 0.11, aver. **0.05**; color values of extract, red 4 to 17, aver. **9**, yellow 21 to 62, aver. **32**, ratio of red to yellow 2.5 to 5.7, aver. **3.4**; color values of lead filtrate, red 0.15 to 0.50,

¹ U. S. Dept. Agr., Bur. Chem. 1912, Bul. **152**.

² J. Ind. Eng. Chem. 1915, **7**, 516.

³ J. Am. Chem. Soc. 1899, **21**, 256.

⁴ U. S. Dept. Agr., Bur. Chem. 1910, Bul. **132**, 110; 1911, Bul. **137**, 120.

⁵ Ibid. 1909, Bul. **122**, 206; 1910, Bul. **132**, 90.

COMPOSITION OF AUTHENTIC VANILLA AND TONKA EXTRACTS (WINTON, BERRY, AND ALBRIGHT)

	Vanillin g. per 100 cc.	Nor- mal Lead No.	Color of Extract			Color of Lead Filtrate *				Amyl alcohol insol. color	Acidity †			Ash: g. per 100 cc.			Alkalinity of Ash ‡		
			R	Y	R : Y	R	Y	R : Y	R	Y	Total	Of va- nillin	Not va- nillin	Total	H ₂ O sol.	H ₂ O insol.	Total	H ₂ O sol.	H ₂ O insol.
Mexican	0.15	0.47	19	55	2.6	1.0	4.8	4.0	4	5	19.0	10	27	0.297	0.246	0.037	36	29	7
	Min.	0.68	56	154	3.8	2.0	8.0	5.6	6	9	24.4	13	42	0.422	0.349	0.073	53	40	13
	Max.	0.17	32	97	3.1	1.5	6.5	4.5	5	7	21.2	11	35	0.359	0.301	0.058	45	35	10
Bourbon	0.13	0.44	22	65	2.3	1.4	5.8	2.8	4	5	21.3	8	22	0.263	0.220	0.043	35	25	9
	Min.	0.63	55	127	3.9	2.4	8.2	5.0	8	10	30.3	14	38	0.373	0.319	0.080	47	34	18
	Max.	0.18	30	94	3.2	1.0	7.0	3.8	6	8	26.6	11	29	0.317	0.259	0.058	40	27	13
Seychelles	0.16	0.45	22	77	2.5	1.0	5.0	4.0	4	6	22.7	10	22	0.251	0.213	0.038	34	24	9
	Min.	0.60	50	162	3.6	3.4	14.6	5.0	7	9	29.4	13	30	0.316	0.262	0.058	47	30	17
	Max.	0.19	33	107	3.2	1.8	7.9	4.5	5	8	25.6	12	27	0.293	0.243	0.050	39	27	12
Madagascar	0.16	0.40	25	85	2.7	1.4	6.2	3.5	4	6	23.2	10	26	0.220	0.193	0.027	34	26	8
	Min.	0.63	47	148	3.5	2.6	11.5	5.1	7	9	30.3	20	35	0.326	0.271	0.060	46	33	14
	Max.	0.22	34	111	3.2	2.0	8.7	4.5	6	8	26.8	14	31	0.284	0.239	0.045	39	28	11
Comores	0.12	0.40	22	70	2.8	1.4	6.0	3.4	5	6	20.4	8	14	0.229	0.182	0.037	33	22	9
	Min.	0.31	40	140	3.8	2.6	12.6	5.3	8	9	30.3	20	39	0.432	0.357	0.081	54	38	17
	Max.	0.18	31	99	3.2	1.9	7.7	4.1	6	8	26.7	12	28	0.333	0.272	0.061	45	31	14
So. American	0.19	0.49	42	117	2.5	1.8	6.8	3.5	4	6	20.0	12	32	0.305	0.261	0.044	38	26	12
	Min.	0.23	50	155	3.1	2.6	10.4	4.0	6	6	29.4	15	37	0.344	0.295	0.054	42	30	12
	Max.	0.21	46	134	2.9	2.3	8.5	3.8	5	6	23.3	14	35	0.325	0.276	0.049	40	28	12
Ceylon	0.07	0.57	40	145	3.2	1.4	6.4	4.1	4	4	22.7	4	28	0.361	0.313	0.048	43	33	10
	Min.	0.67	61	195	3.6	7.6	32.6	4.6	12	17	50.0	5	45	0.443	0.386	0.060	56	44	12
	Max.	0.08	48	162	3.4	4.3	18.2	4.3	8	11	36.1	5	34	0.409	0.354	0.055	49	38	11
Java	0.22	0.44	44	130	3.0	2.4	10.4	4.1	5	6	32.2	14	30	0.290	0.246	0.044	38	31	7
	Min.	0.61	45	177	3.9	3.2	13.4	4.3	7	10	35.7	15	37	0.349	0.299	0.050	49	38	11
	Max.	0.23	44	150	3.4	2.9	12.1	4.2	6	8	34.5	15	33	0.311	0.265	0.046	42	34	8
Tahiti	0.11	0.44	15	40	2.7	0.6	3.1	5.2	4	7	16.0	7	23	0.221	0.179	0.039	30	23	7
	Min.	0.50	17	50	3.0	0.6	3.5	5.8	4	8	18.8	7	26	0.288	0.249	0.042	37	29	8
	Max.	0.11	16	45	2.9	0.6	3.3	5.5	4	8	17.4	7	24	0.254	0.214	0.040	33	26	7
Vanillons	0.06	0.52	42	107	2.5	1.4	6.6	4.7	3	3	22.2	4	34	0.263	0.214	0.048	38	30	7
	Min.	0.11	5	18	3.6	0.5	2.4	4.8	10	13	30.3	5	5	0.163	0.156	0.007	16	14	2
	Max.	0.11	5	19	3.8	0.5	2.4	4.8	10	13	31.2	5	5	0.132	0.122	0.010	15	12	3
Tonka Beans	0.11	0.11	5	19	3.7	0.5	2.4	4.8	10	13	30.8	5	5	0.147	0.139	0.008	15	13	2
	Min.	0.11	5	19	3.7	0.5	2.4	4.8	10	13	30.8	5	5	0.147	0.139	0.008	15	13	2
	Max.	0.11	5	19	3.7	0.5	2.4	4.8	10	13	30.8	5	5	0.147	0.139	0.008	15	13	2
All Analyses §	0.11	0.40	15	40	2.3	0.6	3.1	2.8	4	5	16.0	7	14	0.220	0.179	0.027	30	22	7
	Min.	0.31	56	177	3.9	3.4	14.6	5.8	8	10	35.7	20	42	0.432	0.357	0.081	54	40	18
	Max.	0.19	32	102	3.2	1.8	7.6	4.2	6	8	25.5	12	30	0.319	0.265	0.054	42	30	12

§ Evaporated Vanilla Beans

aver. **0.27**, yellow 0.8 to 2.2, aver. **1.2**, ratio of red to yellow 3.0 to 6.5, aver. **4.6**; per cent of total color in lead filtrates, red 2 to 7, aver. **3**, yellow 2 to 6, aver. **4**.

Influence of Grade and Length of Bean.—Tabulated below are the average results obtained by Winton and Berry ¹ by grade and by length of the bean, excluding South American, Java, Ceylon, and Tahiti because of the small number of samples or abnormal composition. Passing from the lowest to the highest grades there is a marked increase of vanillin and a marked decrease of normal lead number and color value. Tahiti beans yield an extract low in vanillin and color but intermediate in normal lead number. The conclusions reached apply only to the different grades of the same or related varieties. The slight increase in vanillin and decrease in normal lead number from the shortest to the longest beans may indicate a corresponding inferiority of the shorter beans.

AVERAGE COMPOSITION OF VANILLA EXTRACTS MADE FROM DIFFERENT GRADES AND LENGTHS OF VANILLA BEANS (WINTON AND BERRY)

	Sam- ples	Va- nil- lin†	Nor- mal Lead No.	Color of Extract			Color of Lead Filtrate*					Amyl alco- hol insol. color‡
				R	Y	R:Y	R	Y	R:Y	R‡	Y‡	
Grade:						1:			1:	%	%	%
First.....	14	0.20	0.49	24	77	3.2	1.5	6.1	4.2	6	8	25.7
Second.....	10	.20	.53	31	92	3.1	1.7	7.2	4.4	6	8	25.3
Third.....	16	.19	.55	32	104	3.3	1.8	7.6	4.3	6	7	25.7
Fourth.....	15	.17	.58	35	113	3.2	2.1	8.7	4.1	6	8	26.8
Fifth.....	5	.15	.59	35	111	3.1	1.9	7.5	4.0	5	7	22.5
Length:												
20-23 cm.....	19	0.20	0.52	30	99	3.3	1.8	7.6	4.3	6	8	25.3
15-19 cm.....	27	.18	.55	32	100	3.2	1.7	7.2	4.3	6	7	25.4
10-14 cm.....	17	.18	.56	33	104	3.2	2.1	8.4	4.1	6	8	27.8

* Calculated to volume of extract. † G. per 100 cc. ‡ Per cent of total color.

Influence of Different Menstrua.—Winton and Berry ¹ determined the usual constituents in extracts made (1) with and without sugar, (2) with glycerin substituted for sugar, and (3) with 35 per cent alcohol substituted for the 60 per cent. The U.S.P. method of preparation was followed so far as the nature of the substitution permitted. When glycerin was used, it was mixed at the outstart with the ground

¹ Loc. cit.

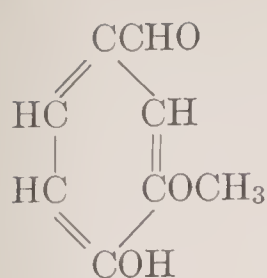
beans. Alcohol of 35 per cent was highly unsatisfactory since it extracted gelatinous matter which clogged the percolator. The weaker alcohol had little influence on the vanillin content but gave higher normal lead numbers, lower color values of the extract, and higher percentage of color remaining both in the lead filtrate and insoluble in amyl alcohol. Glycerin extracts were more strongly colored than the others; a second extraction, however, removed little color where glycerin had been used, but brought the others up to the same degree of color. The results follow:

COMPOSITION OF VANILLA EXTRACTS MADE WITH DIFFERENT MENSTRUUA
(WINTON AND BERRY)

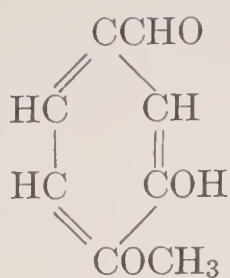
Kind of bean and menstruum	Vanillin†	Normal Lead No.	Color of Extract			Color of Lead Filtrate*					Amyl alcohol insol. color‡
			R	Y	R:Y	R	Y	R:Y	R‡	Y‡	
					1:			1:	%	%	%
Mexican:											
60% alcohol.....	0.19	0.70	33	103	3.1	1.8	7.1	3.9	5.5	6.9	18.6
60% alcohol and sugar (U. S. P.).....	.19	.65	35	103	2.9	2.0	8.6	4.3	5.7	8.4	24.4
60% alcohol and glycerin	.16	.69	41	123	3.0	2.0	8.8	4.4	4.9	7.2	22.7
35% alcohol.....	.17	.82	31	75	2.4	1.8	6.6	3.7	5.8	8.8	27.8
35% alcohol and sugar...	.17	.79	28	75	2.4	2.0	7.5	3.8	7.1	10.0	38.5
35% alcohol and glycerin	.18	.80	40	90	2.3	2.0	7.5	3.8	5.0	8.3	35.7
Bourbon:											
60% alcohol.....	.19	.61	34	108	3.2	1.9	8.2	4.3	5.6	7.6	20.5
60 per cent alcohol and sugar (U. S. P.).....	.19	.57	39	119	3.1	2.4	10.0	4.2	6.2	8.4	25.1
60% alcohol and glycerin	.20	.58	43	133	3.1	2.0	9.6	4.8	4.7	7.2	25.0
35% alcohol.....	.17	.71	30	73	2.4	1.8	7.0	3.9	6.0	9.6	34.5
35% alcohol and sugar...	.17	.66	31	78	2.4	2.2	8.0	3.6	7.1	10.3	45.4
35% alcohol and glycerin	.19	.68	50	110	2.2	2.4	8.4	3.5	4.8	7.6	38.5
Tahiti:											
60% alcohol.....	.11	.43	13	40	3.1	.6	2.6	4.3	4.6	6.5	14.3
60% alcohol and sugar (U. S. P.).....	.11	.44	15	40	2.7	.6	3.1	5.2	4.0	7.7	16.0
60% alcohol and glycerin	.11	.43	24	53	2.2	.7	3.3	4.7	2.9	6.2	15.9
35% alcohol.....	.09	.39	15	30	2.3	1.2	4.0	3.3	8.0	13.3	23.8
35% alcohol and sugar...	.09	.44	15	33	2.2	1.3	4.4	3.4	8.7	13.9	28.6
35% alcohol and glycerin	.10	.40	15	33	2.0	.9	3.3	3.6	6.0	10.0	24.4

* Calculated to volume of extract. † G. per 100 cc ‡ Per cent of total color.

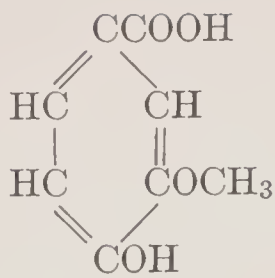
CONSTITUENTS.—Vanillin or Methylprotocatechuic Aldehyde, $C_8H_8O_3$ or $C_6H_3(CHO)(OCH_3)(OH)$.—The hydroxyl and methyl groups are at 3 and 4, respectively, whereas in isovanillin their position is reversed. Both are derivatives of vanillic acid.



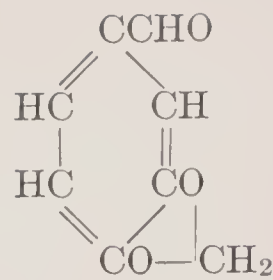
Vanillin



Isovanillin



Vanillic Acid



Heliotropin

To facilitate comparison, the CHO and O₂CH₂ groups of heliotropin are placed at 1 and 3,4 respectively, as adopted by Chemical Abstracts, rather than at 3 and 5,6, as given by the pioneers Doebner,¹ Ladenburg and Scholtz,² and Scholtz³ and recently by Small.⁴

Vanillin crystallizes as long, narrow prisms or needles, melting at 80 to 81° C., soluble in about 100 parts of cold water and readily in alcohol, ether, chloroform, and petroleum ether. It has a slight acid reaction. Winton, Albright, and Berry⁵ found that 1 gram neutralizes 63.0 cc. of N/10 alkali, using phenolphthalein as indicator, which is somewhat below the theoretical amount, 65.8 cc., and that sugar, glycerin, and caramel do not influence the result.

Vanillin occurs in various orchidaceous fruits, also in small amount in Sumatra benzoin, in sugar beets, in asafoetida, and, so it is stated, in potato parings. It is prepared from the alcohol or ether extract of vanilla beans by various methods depending on solution in water, sublimation, or recrystallization.

Synthetic vanillin is prepared from the eugenol of oil of cloves by oxidation, from guaiacol by treatment with chloroform and sodium hydroxide, from coniferin by oxidation, and by various other processes.

From an alcoholic extract of green vanilla beans, Goris⁶ separated a glucoside, *glucovanillin*, as crystals melting at 192° C. and with a specific rotation of -88.3, and from the mother liquor *glucovanillic alcohol*. He considers that glucovanillic alcohol is first formed, then from it by oxidation glucovanillin, and finally vanillin. A third glucoside, yielding on hydrolysis a fragrant ether, was also found to be present.

Vanillic Acid or *m*-Methylprotocatechuic Acid, C₈H₈O₄ or C₆H₃(COOH)(OCH₃)(OH).—See also structural formula above.

¹ Ber. 1890, **23**, 2375.

² Ibid. 1894, **27**, 2958.

³ Ibid. 1895, **28**, 1187.

⁴ Gilman: Organic Chemistry, New York, 1938, p. 1033.

⁵ Loc. cit.

⁶ Compt. rend. 1924, **179**, 70.

It melts at 207° C. and is odorless.

Heliotropin, Piperonal, or Methyleneprotocatechuic Aldehyde, $C_8H_6O_3$ or $C_6H_3(CHO)(O_2 : CH_2)$.—See also structural formula above and Piperic Acid, p. 332.

Closely allied to vanillin is this odorous substance which occurs naturally in heliotrope flowers. It may be synthesized from potassium piperate and potassium permanganate, but is now manufactured from safrole, $C_6H_3(C_3H_5)(O_2 : CH_2)$, for the perfumery industry. Certain varieties of vanilla beans—perhaps all varieties—contain considerable amounts of heliotropin. It is stated that the Tahiti bean contains more heliotropin than vanillin. It crystallizes as lustrous prisms melting at 37° C. and boiling at 263° C. It is difficultly soluble in water (500 to 600 parts), but readily soluble in alcohol and ether.

Resins.—The term resins has been loosely applied to constituents of vanilla beans, other than vanillin, which dissolve in 60 per cent alcohol and precipitate on dealcoholizing. Hess¹ acidifies the dealcoholized solution and, after the resin has completely separated, decants off the clear liquid and collects the precipitate on a weighed filter, washes, dries, and weighs, or else he subjects the precipitate without drying to certain tests. He states that the precipitate dissolves in dilute alkali to a red liquid and is reprecipitated on acidifying; also that the alcoholic solution of the precipitate gives no marked color change with ferric chloride solution or hydrochloric acid.

These tests do not always give the same results and at best convey little idea of the nature of the resins.

Pentosans.—In the dry matter Hanus and Bien² found 5.48 per cent.

Mineral Constituents.—Busse³ quotes the following analysis of the ash of vanilla beans by Leutner:⁴

K ₂ O	Na ₂ O	CaO	MgO	Fe ₂ O ₃	Al ₂ O ₃	P ₂ O ₅	SO ₃	SiO ₂	Cl	CO ₂
%	%	%	%	%	%	%	%	%	%	%
16.21	6.68	19.66	9.61	0.26	4.66	9.45	0.10	0.17	0.50	28.28

¹ J. Am. Chem. Soc. 1899, **21**, 721.

² Z. Unters. Nahr.-Genussm. 1906, **12** 395.

³ Arb. kais. Gesundh. 1898, **15**, 1.

⁴ Pharm. Z. Russland 1871, **10**, 642.

FRUITS OF THE PEPPER FAMILY

(*Piperaceæ*)

PEPPER (including black and white) is the most important spice, long pepper is one of the least important, and cubebs are a drug and sometime pepper adulterant.

COMPARATIVE MACROSCOPIC STRUCTURE. Neither calyx nor corolla is present, each *flower* being borne in a shield-shaped bract extended and curved in such a manner as to cover also the sides of two or three neighboring flowers. The *fruit* is one-seeded; the *seed* is orthotropous.

Pepper berries are sessile in spikes; long pepper is an elongated compound fruit; cubebs are borne on individual stems which, however, are not pedicels but the elongated base of the pericarp.

Reserve starch in this group is in the bulky *perisperm*, the endosperm and embryo being minute.

COMPARATIVE MICROSCOPIC STRUCTURE.—All three products have *stone cells* in the hypoderm, *oleoresin cells* in the outer and inner mesocarp, and minute *starch grains* in aggregates in the perisperm. *Oleoresin cells* occur also in the perisperm of pepper and cubebs. The *endocarp* of pepper consists of cells with thickened radial and inner walls (beaker cells), that of long pepper of elongated, beaded cells, and that of cubebs of stone cells. The *spermoderm* of all three products consists of three thin layers.

The *piperine* of pepper and long pepper, likewise the *cubebin* of cubebs, give with sulphuric acid a red color by direct treatment and a blue color after previous soaking in ammonium molybdate.

PEPPER

Piper nigrum L.

Fr. Poivre. Sp. Pimienta de Castilla. It. Pepe. Ger. Pfeffer.

Pepper is the berry of a woody vine growing native on the Malabar coast in India. It is cultivated throughout the East Indies especially in Sumatra, and sparingly in the West Indies.

The history of pepper in ancient and medieval times is replete with romance, superstition, adventure, exploration, and maritime commerce, but is marred during the Victorian period by widespread adulteration, detected by microscopical and chemical examination carried out in the enforcement of food laws. At times in the Middle Ages it was worth its weight in gold; today it costs each consumer but a few cents a year. Whether because its flavor blended admirably with that of meat and vegetables or because it covered that of taint, or for both reasons, pepper grew in popularity with the years until today it is regarded as a household necessity.

Whole pepper berries or "pepper corns" are added to pickles and certain types of sausage and are ground in miniature mills at the table, but the great bulk of the product is ground before marketing for consumption.

Black Pepper is the berry of the pepper vine picked before ripening and dried either in the sun or over fires. It is more pungent than white pepper and is generally preferred in the United States.

Tellicherry is today the leading black pepper of India. Allepy and Mangalore are other Indian varieties. Singapore (the port of shipment), Lampong, and Acheen are commercial varieties grown in Sumatra.

Impurities and Diluents.—The common impurities of whole black pepper are stems, pepper shells (often the husks of empty kernels), and dirt. The admixture to unground pepper of artificial pepper corns and fruits or seeds of various species such as *Embelia ribes* Burn., pepper tree (*Schinus molle* L.), juniper berries (*Juniperus communis* L.), various legumes, etc., has been reported by European analysts, but it is doubtful if any of these ever was present in pepper sold in the United States. Ground black pepper, however, was formerly subject to gross adulteration with a great variety of foreign materials. The writers have detected in official samples from the retail market charred cocoanut shells, olive stones, buckwheat hulls, charcoal, weed seeds, wheat products, biscuit, maize products, peas, mustard hulls, pepper shells (obtained in the preparation of white pepper and in cleaning black pepper), and dirt.

White Pepper is the fruit of the pepper plant, picked when fully ripe, from which the outer pericarp has been removed by attrition with or without preliminary fermentation or soaking. The flavor is less pungent than that of black pepper, but whether it is more desirable is a matter of opinion; epicures delight in it, but to the untrained nostril it suggests carrion. White pepper is more commonly used in

Europe than in America. The grades on the market include Singapore, Siam, and Penang, the last being commonly coated with a mixture consisting chiefly of carbonate of lime.

Diluents at one time added to white pepper included every imaginable inert, light-colored powder of vegetable origin such as ground olive stones, cereal meal (notably wheat, rice, Indian corn, and buckwheat), ground peas, and various leguminous powders.

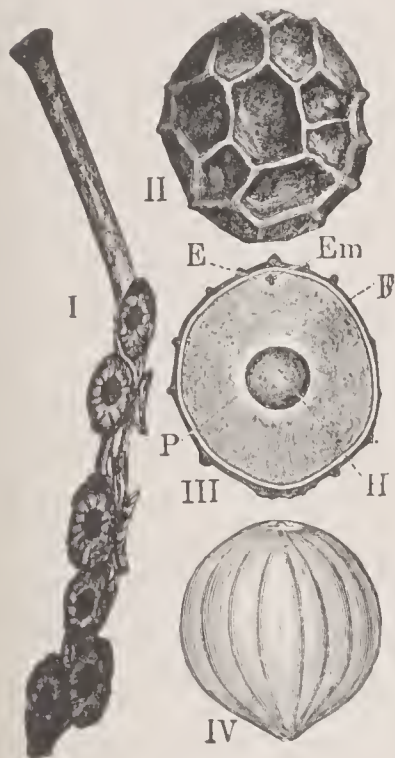


FIG. 67.

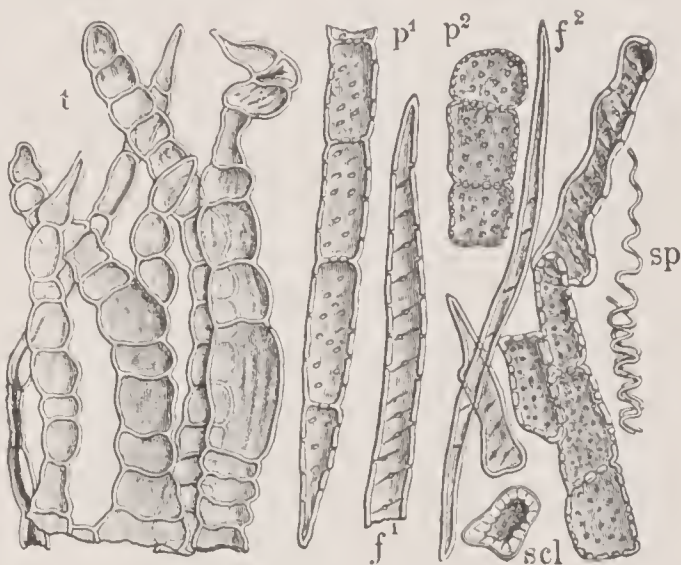


FIG. 68.

FIG. 67.—Pepper. I stem (peduncle, rachis, and bracts). II black pepper, entire. III black pepper in longitudinal section: *F* shell (separates at white line in preparing white pepper); *P* perisperm; *E* endosperm; *Em* embryo; *H* central cavity. IV white pepper showing bundles. $\times 4$. (A.L.W.)

FIG. 68.—Pepper Stems. Elements in surface view. *f*¹, *f*² bast fibers; *p*¹, *p*² wood parenchyma; *scl* sclerenchyma cells; *sp* spirals of vessels; *t* hairs from bracts. $\times 160$. (A.L.W.)

Decorticated White Pepper differs from ordinary white pepper in that all the coats of the berry down to the perisperm have been removed. The process is commonly carried out by the spice importer or grinder.

MACROSCOPIC STRUCTURE (Fig. 67).—Peppercorns are produced in drooping spikes resembling bunches of currants. The *stems* (*I*), including peduncle, rachis, and the peculiar bracts which nearly cover the flowers during blooming, often occur in the commercial

product. When ripe the *fruit* is red, about the size of a currant. The color changes to black on drying and the surface becomes wrinkled (*II*). The shelled fruit (white pepper) is light buff, globular or ovoid, with a slight elevation at the base, another elevation at the apex arising from a slight depression, and ten to fifteen fibro-vascular bundles forming meridianlike markings (*IV*).

A longitudinal section (*III*) shows that the pericarp (*F*) and spermoderm are relatively thin and that by far the greater part of the fruit consists of a starchy mass—the perisperm (*P*). As is true of the endosperm of the cereals, the mass is partly horny and partly floury, the proportion differing greatly in different samples. A hollow cavity (*H*), usually central, may or may not be present in black pepper, but is the rule in white pepper. At the apex of a carefully prepared median longitudinal section the minute embryo (*Em*) embedded in a small endosperm (*E*) may be seen under a lens, although both are more clearly defined in a microscopic section (Fig. 73).

MICROSCOPIC STRUCTURE. Peduncle.—Karsten, also De Candolle, among earlier botanists showed that the *fibro-vascular bundles* of the *Piperaceæ* were intermediate between the endogenous and the exogenous types. A cross section of the pepper peduncle shows an outer ring of bundles and several bundles in the pith. Both types are accompanied by bast fibers. Large cavities also occur in the pith. Weiss,¹ elaborating the idea of Karsten, shows that the fibro-vascular bundles are leaf traces which pass first from leaf to the outer bundle ring, then in the next internode move into the pith and finally join with others to form larger pith bundles.

Bast fibers (Fig. 68, *f*¹, *f*²), of the usual type with pointed ends and blunt forms, both with diagonal pores, are numerous in the bundle strands. The sclerenchymatous ground tissue of the cortex contains *wood parenchyma* (*p*¹, *p*²), the cells being arranged in longitudinal rows often with pointed members at the ends. Transitions to stone cells (*scl*) are common. *Spiral vessels* (*sp*) are numerous.

Bracts.—As first noted by Hanausek,² jointed and sometimes branching *hairs* (Fig. 68, *t*) occur on the epiderm.

Pericarp (Fig. 69, *F*; Figs. 70 and 71).—Seven layers are present, of which four may be grouped as mesocarp: (1) *epicarp* (*epi*) of polygonal cells, containing dark brown contents, and stomata; (2) *hypoderm* (*hy*) of polygonal, thin-walled cells, in one or two rows, and groups of radially elongated stone cells with dark contents; (3)

¹ Flora 1876, p. 321.

² Z. Nahr.-Unters. Hyg. 1889, 3, 59.

outer mesocarp (*mes*¹) of polygonal cells interspersed with *oleoresin* cells (*res*); (4) *fibro-vascular bundle zone* (*mes*²) or middle mesocarp, the cells being longitudinally elongated about the fibro-vascular bundles (*fv*); (5) *oil zone* (*mes*³) of large polygonal cells containing oil drops (*ol*); (6) *porous cells* (*mes*⁴), in one or two rows, with thin but sclerenchymatized walls and (7) *endocarp* (*end*) of beaker cells with strongly thickened radial and inner walls.

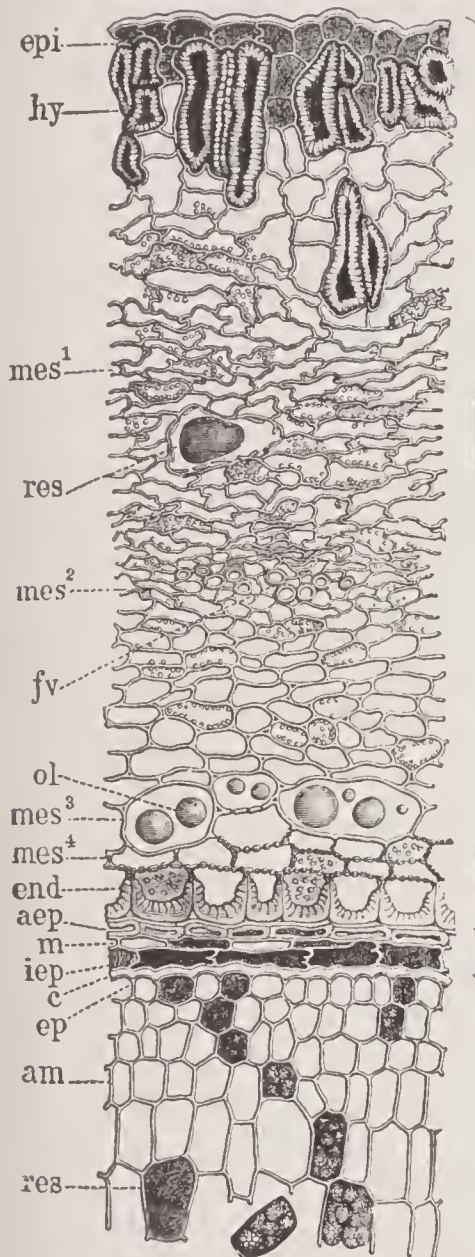


FIG. 69.

FIG. 69.—Pepper. Cross section. *F* pericarp: *epi* epicarp; *hy* hypoderm; *mes*¹ outer starchy mesocarp with *res* oleoresin cell; *mes*² starchy mesocarp with *fv* bundle; *mes*³ oily mesocarp with *ol* oil globules; *mes*⁴ porous mesocarp; *end* endocarp (beaker cells). *S* spermoderm: *aep* outer epiderm; *m* middle layer; *iep* inner epiderm. *P* perisperm: *ep* epiderm (aleurone cells) with *c* cuticle; *am* starch cells; *res* oleoresin cell. $\times 160$. (A.L.W.)

FIG. 70.—Pepper. Elements of outer pericarp in surface view. Reference letters as in Fig. 69. $\times 160$. (A.L.W.)

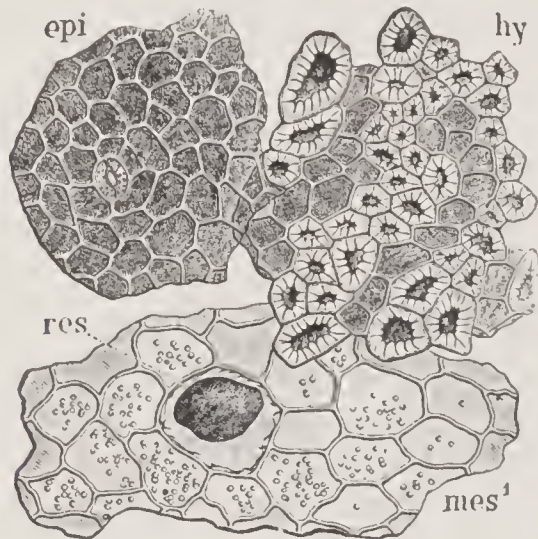


FIG. 70.

iodine and deep red with safranin. The cell walls of the remaining layers stain blue with chlorzine iodine and light red or red-brown with safranin.

The ill-defined contents of the outer and middle mesocarp include disorganized chlorophyll grains, minute starch grains, volatile oil, resin, and piperine.

Plahl¹ found two kinds of *crystals* in or near the bundle zone: (1) small crystals of calcium oxalate about the size of the starch grains, and (2) large crystals of magnesium oxalate, the size of the stone cells, which gave positive tests with sodium phosphate and calcium chloride solutions, both in the presence of ammonium hydroxide and ammonium chloride. Ossowski,² depending on microchemical tests, claims that calcium carbonate crystals occur in the pericarp.

In preparing white pepper the separation is through the *fibro-*

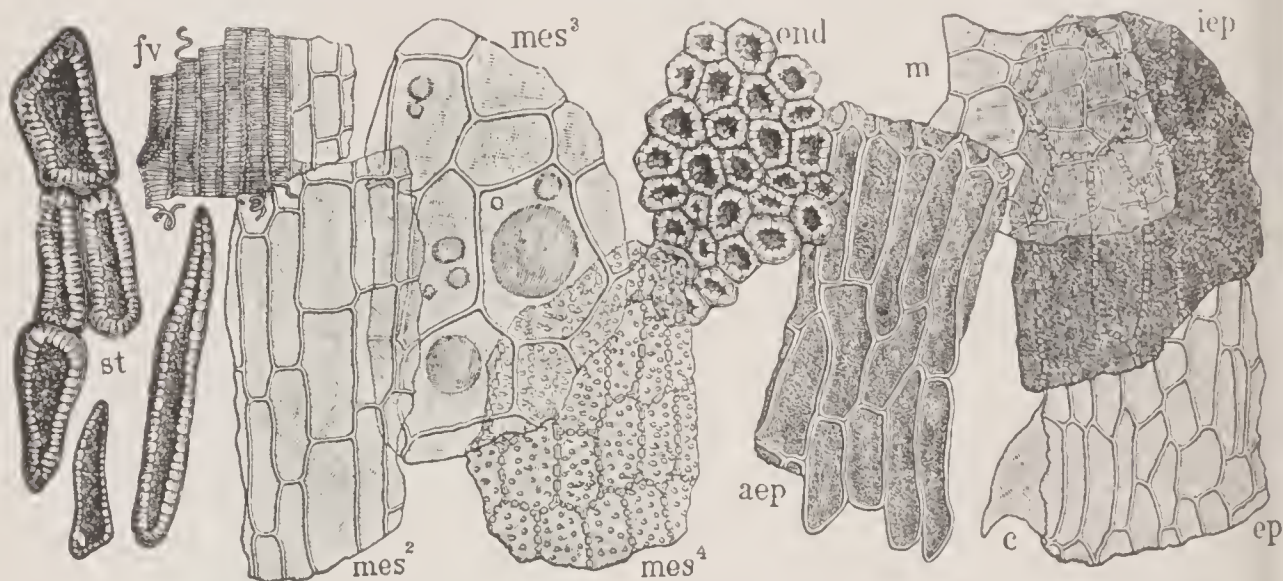


FIG. 71.—Pepper. Elements of inner pericarp and seed in surface view. *st* stone cells from base. Other reference letters as in Fig. 69. $\times 160$. (A.L.W.)

vascular bundle zone (*mes²*). At the base of the kernel occur elongated *stone cells* (Fig. 71, *st*).

Spermoderm (Fig. 69, *S*; Figs. 71, 72, and 73).—After careful treatment of cross and longitudinal sections with Labaraque's solution and mounting in chlorzinc iodine three layers are evident, but in parts, particularly at the apex, the middle coat is absent or obscured: (1) *outer epidermis* (*aep*) of longitudinally elongated cells, passing into isodiametric forms at the apex, with a cuticle (staining yellow), swollen walls, and medium dark contents; (2) *middle coat* (*m*) of characterless cells; and (3) *inner epidermis* (*iep*) of longitudinally elongated cells, passing into palisade cells at the apex, with porous (beaded) walls and dark brown contents.

¹ Arch. Chem. Mikros. 1912, 5, 320.

² Roczniki Farm. 1922, 1, 185.

The description of *spermoderm* (above) as well as of *perisperm* (below) and the cuts showing the structure are the result of recent extensive studies which fully verify the conclusions reached by one of us after studies carried out soon after 1900.¹

Tschirch and Oesterle² in their longitudinal section through the micropyle show the two layers of the spermoderm present in that region, also the cuticle of the perisperm, but the separation of the two cell layers in their illustration, as well as their description, shows that they consider the outer epiderm as part of the pericarp.

Vogl³ with good reason regards the beaker cells as endocarp and shows two layers of spermoderm, although in his illustration of surface mounts the outer and inner epiderms appear to be reversed.

Wallis⁴ shows three layers within the beaker cells, but he concludes that the outer belongs to the pericarp and the two inner to the spermoderm. The innermost of these layers, which we find has the characters of a cuticle with wrinkles at the apex of the kernel, he regards as cellular tissue, although parts of his own cut of a longitudinal section at the apex show what appear to be wrinkles rather than cell walls. The appearance of a cell in longitudinal section is often stimulated when the top turn of one wrinkle and the bottom turn of another are seen together in a section. In surface view (Fig. 72, C) the resemblance to cells is still more striking.

The presence of a cuticle over the layer adjoining the beaker cells is proof that here pericarp ends and spermoderm begins, and the inner

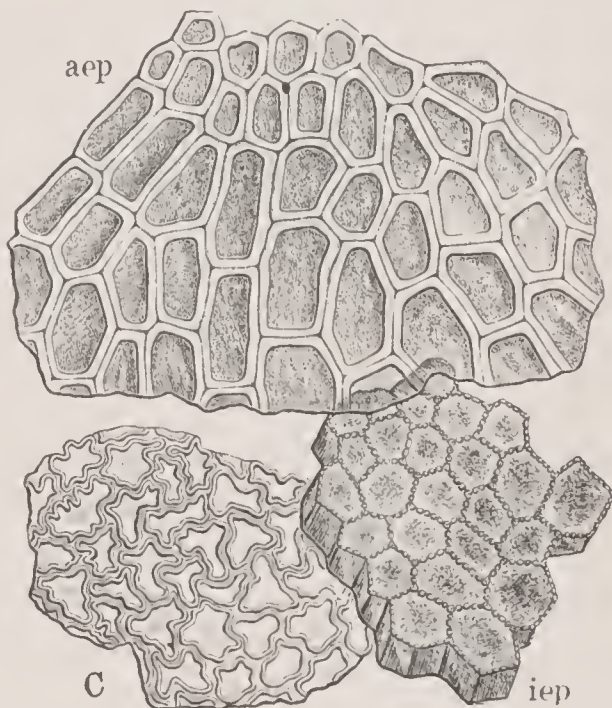


FIG. 72.—Pepper. Apex tissues in surface view. Spermoderm: *aep* outer epiderm; *iep* inner epiderm. Perisperm: *C* cuticle. $\times 160$. (A.L.W.)

¹ See Pepper: Moeller's Mikros. Nahr.-Genussm., Berlin, 2 Aufl. 1905; Winton's Micros. Veg. Foods, New York, 1st Ed. 1905 and 2nd Ed. 1916.

² Anat. Atlas, Leipzig, 1900, p. 105.

³ Wicht. Nahr.-Genussm., Berlin, 1899, p. 395.

⁴ Analyst, 1915, 40, 190.

cuticle marked by wrinkles at the apex likewise is a division line separating in this case spermoderm from perisperm.

Perisperm (Figs. 69 and 73, *P*).—Pepper is one of the few fruits with reserve material chiefly in the perisperm. Over the body of the grain the *epiderm* (*ep*) consists of isodiametric or more commonly longitudinally elongated cells with a thick cuticle (*c*) staining yellow by the above test. The *epiderm* and often one or more rows of *sub-epidermal cells* (isodiametric in cross section) contain protein matter with little or no starch. Further inward the cells are radially elon-

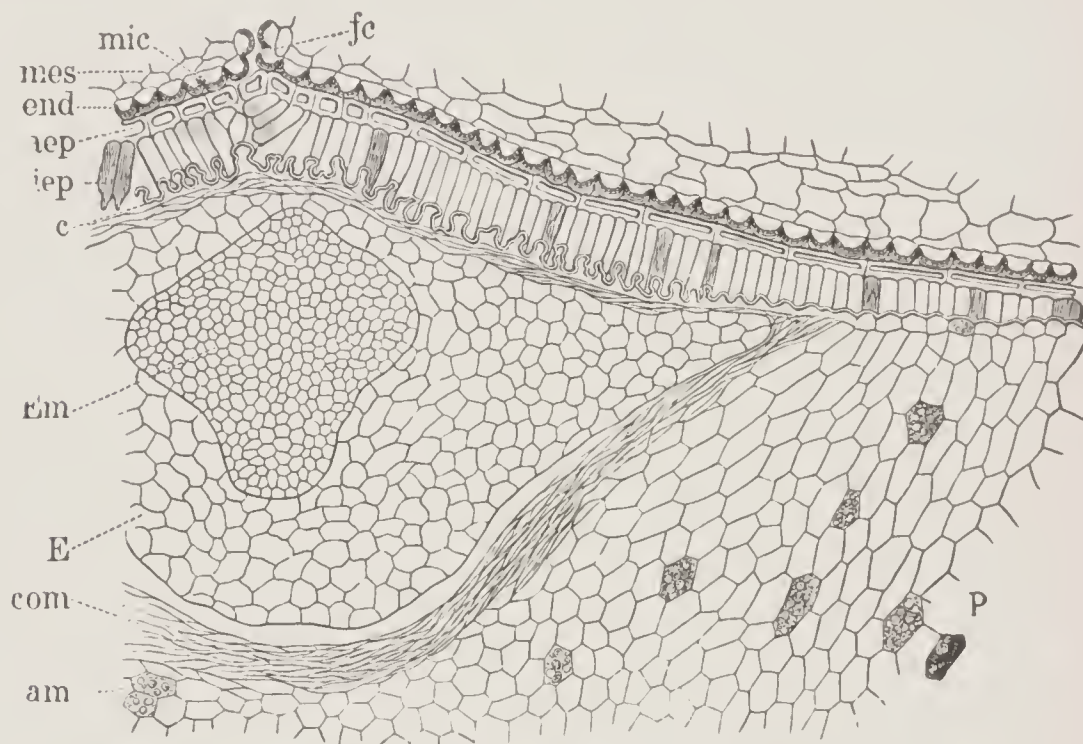


FIG. 73.—Pepper. Longitudinal section. *E* endosperm; *Em* embryo; *P* perisperm with *am* starch cells and *com* compressed cells; *fc* fruit canal; *mic* micropyle. Other reference letters as in Fig. 69. $\times 80$. (A.L.W.)

gated and most of them contain abundant *starch* (*am*) in rounded aggregates of various sizes or masses. Analogous to the starch in the endosperm of cereals, the starch in the horny perisperm is embedded in a protein matrix, the whole contents of a cell forming a mass which often separates intact on grinding.

The *starch grains* are minute, usually less than $4\ \mu$ and rarely reaching $6\ \mu$, yet with high magnification they show a distinct hilum. Many of the grains, being from aggregates or starch masses, are angular.

Here and there *oleoresin cells* (*res*) are conspicuous because of their contents which are *resin*, *volatile oil*, *piperine*, and doubtless

other non-starchy substances. Needle-shaped piperine crystals occur in ground pepper.

At the apex of the kernel the perisperm on all sides adjoining the endosperm consists of an obliterated tissue. Whether this condition is due to pressure of active growing tissues or shrinkage during drying, the cuticle of the perisperm, as stated above, becomes strongly wrinkled as appears in longitudinal section and the wrinkles in surface view (like the macroscopic wrinkles on the surface of the pepper corn) simulate cell walls (Fig. 72, *C*).

Endosperm (Fig. 73, *E*).—The cells are polygonal and characterless.

Embryo (Fig. 73, *Em*).—A longitudinal section shows the two minute cotyledons and the upwardly directed radicle. The cells are minute.

CHIEF STRUCTURAL CHARACTERS.—Fruit globular; black pepper wrinkled; white pepper with bundles forming longitudinal markings. Endosperm and embryo minute, at apex of bulky perisperm.

Hypodermal stone cells radially elongated; inner mesocarp with oil cells; endocarp of beaker cells. Perisperm with starch cells containing starch grains up to 6 μ and oleoresin cells.

MICROSCOPY OF GROUND PEPPER.—Only an expert should attempt to detect the presence of added pepper shells in black pepper by microscopic examination, and he should check his findings by chemical analysis. In view of the large number of waste materials which at one time or another have served as adulterants, it is impracticable to give specific instructions for their detection. Such woody products as charred ground cocoanut shells, sawdust, etc., are readily detected by their characteristic stone cells and wood elements. Buckwheat hulls, linseed meal, and other cereal and oil seed products have characteristic microscopic characters described in Volume I. Only light-colored products, such as cereal meal, ground leguminous seeds, and ground olive stone, are commonly added to white pepper. Cereal products and olive stones are described in Volume I, legumes in Volume II. The pungency, reduced by dilution, is sometimes reenforced by the addition of cayenne.

CHEMICAL COMPOSITION.—Many of the analyses of pepper have been made on material of doubtful authenticity and the determinations restricted to ash and sand. Dirt, acquired from dust-laden breezes, spattered mud, or the soil on which the berries are dried by natives, varies greatly with the year and the region, hence unending

disputes between grower and buyer, shipper and consignee, and spice merchant and inspection authorities.

Winton, Ogden, and Mitchell¹ and Winton and Bailey,² in carrying out analyses at the instance of the U. S. Standards Committee, looked beyond the needs of law enforcement and determined certain constituents of general scientific interest. The samples were drawn by the chemist with due precautions from the original packages, three bags being ground in several cases before making the final subdivision. A summary of these analyses appears in the table on the following page save one.

As regards the constituents given in the table, it may be stated that the piperine, being calculated from the nitrogen in the ether extract as determined by the Gunning-Arnold method, includes chavicine, probably some or all of the piperidine, and possibly other ether-soluble nitrogenous substances none of which is present in considerable amount. In the original publications are also given figures for parts of nitrogen in 100 parts of the non-volatile ether extract which varied from 3.29 to 4.06 in black pepper and from 4.05 to 4.45 in white pepper. The volatile oil is that driven off from the total ether extract (dried over sulphuric acid) by heating first at 100° and then at 110° C. as proposed by Richardson,³ while the "fixed oil," which contains little fat or fatty oil but consists largely of piperine and includes resins, is the non-volatile ether extract remaining after removal of the volatile oil. Although the term "fixed oil" is not appropriate in the present instance, it is uniformly used in this work for the extract obtained by the same method from all the spices. The crude starch includes hydrolyzable matter formed by the action of acid on the fibrous and other non-saccharine constituents which are present in greater amount in black than in white pepper. In decorticated white pepper, which consists only of the starchy interior of the kernel, the results on crude and pure starch are nearly identical. Soluble ash represents the portion dissolved after boiling with water; sand is the mineral residue after boiling with 10 per cent hydrochloric acid.

Following are respectively the average weights per 100 kernels and per liter of the different varieties of black pepper given in the table: Singapore 4.89, 476; Lampong 3.59, 511; Mangalore 8.57, 574; Malabar 5.74, 570; Acheen A 3.44, 432; Acheen B 3.35, 407; and Acheen C

¹ Connecticut Agr. Exp. Sta. Rep. 1898, p. 184; 1899, p. 100.

² Ibid. 1903, p. 158.

³ U. S. Dept. Agr., Div. Chem. 1887, Bul. 13, II, 165.

3.10, 330 grams. The corresponding average values found for white pepper follow: Decorticated 2.77, 773; Singapore 4.41, 608; Tellicherry 6.67, 650; Alleppy 4.21, 588; Siam 4.77, 688; and Penang 5.19, 673 grams.

The weight of 100 kernels varies with the variety, being dependent partly on size and partly on density. As regards the density, some varieties of black pepper, such as Tellicherry, Lampong, Mangalore, and Malabar, have hard solid kernels, while others, such as Singapore and Acheen, particularly the lower grade, are often hollow, crushing readily between the fingers. This property is brought out by the weight of 1 liter.

Doolittle¹ analyzed no less than 45 samples of black pepper, 25 of white pepper, 3 of long pepper, and 4 of pepper shells. In some cases the entire contents of a bag was ground before sampling; this work, however, was done by laborers in the spice mills and not under the eye of the chemist. The methods followed and the constituents determined were essentially the same as were described in the Connecticut Report and later among the methods of the Association of Official Agricultural Chemists. In the main the results confirm those given in the foregoing table, the most notable exception being the maximum percentages of ash and sand which were respectively 8.04 and 2.59 per cent.

Analyses reported by Härtel and Will² are of special interest because they show percentages of volatile oil by Mann's method,³ dextrose values by Härtel's method,⁴ and resins by a method devised by them. The piperine was determined by a method in essential details the same as proposed by Winton, Ogden, and Mitchell.⁵

The *U. S. Standards* require that black pepper contain not less than 6.75 per cent of non-volatile ether extract, nor 30 per cent of starch; not more than 7 per cent of total ash, nor 1.5 per cent of sand. They further require that white pepper contain not less than 7 per cent of non-volatile ether extract nor 52 per cent of starch; not more than 5 per cent of fiber, 3.5 per cent of total ash, nor 0.3 per cent of sand.

Proteins.—No literature on the individual proteins is available, but the hard flinty structure of the perisperm of the better grades suggests

¹ Michigan Dairy and Food Dept. 1903, Bul. 94.

² Z. Unters. Nahr.-Genussm. 1907, 14, 567.

³ Arch. Pharm. 1902, 240, 149.

⁴ Z. Unters. Nahr.-Genussm. 1907, 13, 667.

⁵ Loc. cit.

COMPOSITION OF BLACK, WHITE AND LONG PEPPER (WINTON ET AL.)

	Water	Pro- tein*	Piper- ine†	Oil, fixed	Oil, vola- tile	Starch, pure‡	Starch, crude§	Fiber	Ash, total	Ash, soluble	Sand
	%	%	%	%	%	%	%	%	%	%	%
<i>Black Pepper:</i>											
Singapore											
Min.....	11.47	12.13	6.11	7.36	0.99	36.81	41.36	10.75	3.09	1.75	0.07
Max.....	12.43	13.81	6.52	7.92	1.10	39.66	43.47	11.67	3.68	2.26	0.15
Aver. (5)...	12.00	12.71	6.31	7.73	1.06	38.51	42.80	11.04	3.49	2.10	0.12
Tellicherry											
Min.....	11.27	11.70	5.50	6.86	0.65	37.01	41.55	12.17	4.14	2.75	0.00
Max.....	11.86	11.88	5.50	7.02	1.02	37.01	41.80	12.23	4.28	2.75	0.02
Aver. (2)...	11.56	11.79	5.50	6.94	1.83	37.01	41.67	12.20	4.21	2.75	0.01
Lampung											
Min.....	10.63	10.50	6.31	7.58	1.11	33.41	37.09	11.57	4.86	2.16	0.48
Max.....	12.17	11.37	7.13	9.05	1.34	37.59	41.42	13.08	6.85	2.67	1.63
Aver. (4)...	11.46	10.91	6.72	8.58	1.22	35.08	39.70	12.37	6.05	2.37	1.08
Mangalore...	11.61	11.87	7.13	9.08	1.50	34.93	10.00	4.23	2.19	0.19
Malabar.....	9.47	12.56	4.89	6.10	1.04	44.83	9.68	3.45	2.26	0.09
Acheen A....	12.09	10.88	7.53	9.17	1.09	33.38	38.17	13.07	5.04	2.78	0.48
Acheen B											
Min.....	11.77	11.75	6.92	8.24	1.15	30.79	36.40	14.09	5.00	2.69	0.83
Max.....	12.95	11.81	7.53	9.03	1.75	33.08	38.25	15.85	6.15	3.04	1.25
Aver. (3)...	12.41	11.79	7.13	8.59	1.49	32.17	37.11	14.80	5.65	2.91	1.08
Acheen C											
Min.....	10.84	12.06	7.53	8.52	1.28	22.05	28.15	16.40	5.40	2.81	0.88
Max.....	12.33	12.56	7.94	9.64	2.20	28.60	35.55	18.25	6.35	3.19	1.26
Aver. (5)...	11.79	12.32	7.74	9.29	1.64	25.76	31.97	17.19	5.99	3.04	1.05
<i>Pepper Waste:</i>											
Shells.....	10.57	14.19	1.83	3.04	0.68	2.30	11.43	32.15	11.91	3.20	4.70
Shells, dust...	10.52	12.94	2.85	4.77	1.06	15.30	21.69	23.61	10.30	2.28	2.88
<i>Long Pepper:</i>	9.47	12.25	4.48	6.61	1.55	39.55	42.88	5.76	5.93	4.20	0.22
<i>White Pepper:</i>											
Decorticated											
Min.....	12.72	10.94	6.52	7.21	0.49	62.73	64.79	0.54	1.03	0.44	0.00
Max.....	13.07	11.13	6.52	7.26	0.63	63.60	64.92	0.66	1.10	0.51	0.02
Aver. (2)...	12.89	11.03	6.52	7.24	0.56	63.16	64.85	0.60	1.06	0.47	0.01
Singapore											
Min.....	13.12	10.94	6.92	7.85	0.90	53.11	56.43	3.95	1.14	0.33	0.09
Max.....	13.82	11.19	6.92	7.94	0.95	54.67	57.00	4.25	1.52	0.34	0.10
Aver. (2)...	13.47	11.06	6.92	7.89	0.92	53.89	56.71	4.10	1.33	0.33	0.09
Tellicherry...	11.13	12.12	5.70	6.68	0.64	60.41	3.94	0.97	0.22	0.00
Alleppy.....	9.47	12.44	6.31	7.28	0.55	57.60	4.54	1.05	0.25	0.04
Siam											
Min.....	12.77	10.44	5.70	6.54	0.58	56.10	58.90	3.49	1.26	0.28	0.04
Max.....	14.47	10.88	5.90	6.81	0.83	56.33	59.10	3.55	1.71	0.46	0.20
Aver. (3)...	13.63	10.69	5.80	6.64	0.69	56.18	59.01	3.52	1.47	0.38	0.07
Penang											
Min.....	13.40	10.82	5.29	6.26	0.62	53.26	56.94	3.70	2.73	0.52	0.11
Max.....	14.19	10.94	5.70	6.36	0.89	54.74	57.35	3.91	2.96	0.80	0.18
Aver. (3)...	13.68	10.88	5.50	6.32	0.76	54.01	57.17	3.80	2.84	0.65	0.15

* Total N less N in fixed oil $\times 6.25$. † N in fixed oil $\times 20.36$. Includes ehavicine. ‡ Diastase method. § Reducing matter, after washing with 10% alcohol and direct inversion of residue, calculated as starch.

COMPOSITION OF PEPPER AND PEPPER SHELLS (HÄRTEL AND WILL)

	Piperine	Resin	Volatile oil	Dextrose value	Fiber	Ash	Sand
	%	%	%	%	%	%	%
Black (15)							
Min.*.....	6.02	0.25	1.94	30.6	13.04	4.08	0.10
Max.*.....	8.81	1.04	3.62	42.7	16.30	5.90	1.85
Min†.....	6.02	0.26	1.94	18.3	13.04	4.08	0.10
Max†.....	9.78	1.04	3.85	42.7	21.91	9.32	2.98
Empty Kernels							
Min.....	4.32	0.94	1.68	4.4	30.44	7.39	0.70
Max.....	6.68	0.96	2.14	5.6	32.60	8.30	1.40
Shells							
Min.....	3.64	1.19	0.80	15.3	24.34	6.67	0.03
Max.....	4.75	1.28	1.03	19.0	26.88	8.30	0.05
White (5)							
Min.....	6.56	0.18	1.39	51.3	4.51	0.80	0.10
Max.....	7.64	0.36	2.42	58.5	6.67	3.64	0.15

*Excluding samples with less than 15% of empty kernels. †All analyses.

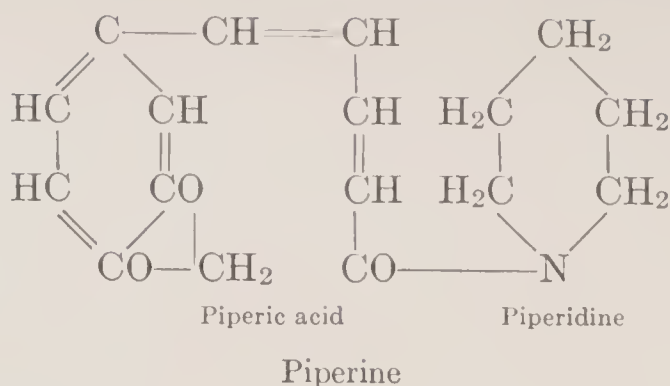
the presence of a matrix of protein matter similar to that in the horny portion of the cereal grains.

Alkaloids. *Piperine*, $C_{17}H_{19}NO_3$ or $CH_2 \cdot O_2 : C_6H_3 \cdot CH : CH \cdot CH : CH \cdot CO \cdot N \cdot C_5H_{10}$.—Oerstedt, the noted Danish scientist, discovered this alkaloid in 1819, and Pelletier in 1821 demonstrated that it reacts as a base. Caseneuve and Caillot,¹ in quantitative determinations, found in black pepper up to 9.15 and in white pepper up to 7.15 per cent. The method followed consisted in boiling the ground pepper with calcium hydroxide, evaporating the mixture to dryness, extracting with ether, evaporating the solvent, and recrystallizing the alkaloid from alcohol. Later authors, both German and American, report somewhat lower percentages.

Rügheimer² showed that piperine is a combination of the base piperidine ($C_5H_{10}NH$) and piperic (piperinic) acid ($C_{12}H_{10}O_4$) into which it may be split up by boiling in alcoholic potash. It may be formed (together with HCl) by heating equal molecules of piperidine and the chloride of piperic acid. Its formula is accordingly as given above or as follows:

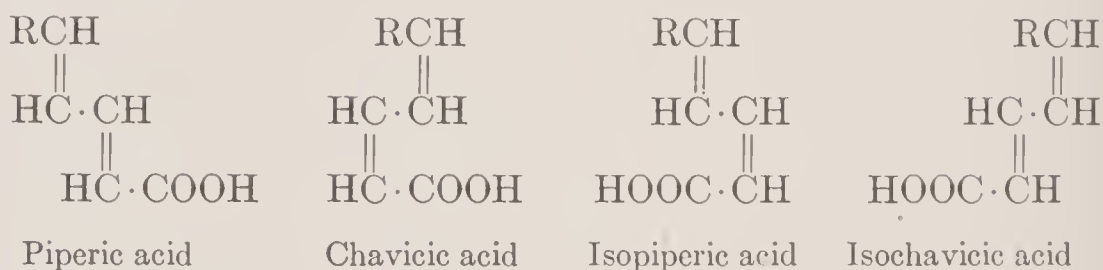
¹ J. pharm. chim. 1877, **25**, 421.

² Ber. 1882, **15**, 1390.



See also Heliotropin.

Ott and Eichler¹ have demonstrated that piperic and chavicic (chavicinic) acids are opposite geometric isomers. These and the two other possible isomers have the following arrangement:



R is the piperonyl group $\text{CH}_2 : \text{O}_2 : \text{C}_6\text{H}_3\text{---}$.

Piperine forms colorless monoclinic, truncated crystals melting at 128 to 130° C., soluble in ether, less so in alcohol, but only slightly soluble in water even at boiling. It dissolves in concentrated sulphuric acid to a red liquid, changing to brown and finally to green-brown. Concentrated nitric acid converts it into a resinous substance which dissolves in dilute potassium hydroxide to a red solution.

Piperine is at first tasteless, but may have a somewhat pungent after-taste. An alcoholic solution, however, is intensely pungent, but Ott and Zimmerman² believe that this is due to resinous matter not completely removed in purification.

Staudinger and Schneider³ have shown that, immediately after grinding with starch, piperine has little taste, even for some hours, but on standing 10 days it develops the sharp taste of pepper. These authors therefore conclude that piperine is the chief pungent principle of pepper, the characteristic taste being due to a reaction with colloidal substances on the tongue and dependent on the proper degree

¹ Ibid. 1922, 55B, 2653.

² Ann. 1921, 425, 314.

³ Ber. 1923, 56B, 699.

of dispersion. This view is corroborated by Rheinboldt¹ who, after subjecting piperine to special purification, thus precluding the presence of resins, found that the alcoholic solution was highly pungent.

Staudinger and Müller² have shown that the piperidides of aliphatic-aromatic acids having 2-, 4-, and 6-CH₂ groups have a more pungent taste than those having 1-, 3-, and 5-CH₂ groups. Riccomanni³ has demonstrated that di-phenyl-pentenoylpiperazine has a pepperlike pungency, especially when mixed with flour, thus indicating that it is not necessary to introduce piperidine into the molecule in order that it may possess a peppery taste.

The idea that piperine is more abundant in pepper shells than in the inner kernel appears to be widespread. The evidence is conflicting, owing in part to calculating all ether-soluble nitrogen as piperine. As a rule analyses show a somewhat greater percentage of piperine in black pepper than in ordinary white pepper and in the lower grades of black pepper containing many soft or empty kernels than in the higher grades with plump hard kernels. On the other hand, pepper shells contain only a fraction as much as whole black pepper; these, however, are removed from the mature kernel, and the process is not merely mechanical, but is said to include soaking in water, which may dissolve some of the piperine and allied substances. Again, decorticated pepper, which contains none of the outer coats, is especially rich in piperine.

Chavicine, C₁₇H₁₉NO₃.—This substance was reported by Buchheim⁴ as occurring in pepper and differing from piperine in being more soluble in alcohol. For many years Buchheim's work lacked confirmation and the substance came to be regarded as of doubtful existence until Ott and Eichler⁵ picked up the thread. The structural relation of chavicic acid to piperic acid, as found by these authors, is described above. A quantity of crude chavicine, equivalent to 0.8 per cent, was isolated from pepper after careful removal of the volatile oil by steam distillation and separation from piperine. On further purification it was shown to be in truth a piperide consisting of piperidine and chavicic (chavicinic) acid. On repeated crystallization from boiling benzol the acid yielded by rearrangement isochavicic acid in

¹ Ibid. 1923, **56B**, 1228.

² Ibid. 1923, **56B**, 711.

³ Atti accad. Lincei 1924, V, **33**, i, 145.

⁴ Arch. exp. Path. Pharmacol. 1876, **5**, 455.

⁵ Loc. cit.

the form of a yellow amorphous granular powder which under the microscope was shown to consist of spherical aggregates, thus distinguishing it from its crystalline isomer piperic acid. Ott and Lüdemann¹ confirmed the work of Ott and Eichler and by hydrolysis separated piperidine and isochavicol acid.

Piperidine or *Hexahydropyridine*, $C_5H_{10} \cdot NH$.—Späth and Engländer² proved that the large amounts of piperidine (black pepper 0.39 to 0.77 per cent; white pepper 0.21 to 0.42 per cent) reported by Johnstone³ are erroneous, owing to the presence of ammonia in the steam distillate which he titrated directly; they found only 0.012 per cent and showed that the substance exists in pepper either as the free base or as a simple salt. They were unable to confirm the presence in the distillate of β -methylpyrrolidine reported by Pictet and Pictet.⁴

Piperidine is a colorless liquid, readily miscible with water and alcohol and boiling at 106 to 108° C. It is strongly basic, combining with mineral and organic acids, and has a biting taste which led some to believe that it is the chief pungent principle of pepper.

Together with piperic acid, piperidine splits off from the piperine of pepper on boiling an alcoholic extract with caustic potash and may be isolated after distillation. It also may be prepared from cadaverine hydrochloride by dry distillation, by electro-reduction of pyridine, and by other processes. By oxidation, piperidine is converted into pyridine.

Other Alkaloids.—Whether piperidides of isopiperic and isochavicol acids are present in pepper does not appear.

Fixed Oil, as noted above, contains relatively little fatty oil. Piperine, the chief constituent, is nitrogenous, hence protein as applied to nitrogen times 6.25 and fat as applied to ether extract in the case of pepper are gross misnomers, since the piperine is included in both. No data on the nature of the fatty oil or resins are at hand.

Volatile Oil.—By Von Fellenberg's chromic acid oxidation method, Zäch⁵ obtained 1 to 3 per cent.

Physical and Chemical Values.—The following physical values are based largely on results obtained by Schimmel & Co.⁶; the chemical values are those by Gildemeister and Hoffmann⁷:

¹ Ber. 1924, **57B**, 214.

² Ibid. 1935, **68B**, 2218.

³ Chem. News 1889, **58**, 235; Analyst 1889, **14**, 41.

⁴ Helv. Chim. Acta 1927, **10**, 593.

⁵ Mitt. Lebensm. Hyg. 1932, **23**, 156.

⁶ Schimmel & Co., Rep. Apr. 1897, table 36.

⁷ Ätherischen Öle, Leipzig, 3 Aufl. 1929, **2**, 457.

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Ester No.	Acetyl No.*	Acid No.
Min.	0.870	1.480	—5	12.0
Max.	0.920	1.500	+3	0.5	22.1	1.1

* Ester number after acetylation.

Constituents.—The nature of the volatile oil is not fully understood. Pictet and Court¹ believe that *methylpyrroline* rather than *piperidine* (see above) is the active volatile alkaloidal constituent. Pictet and Pictet² isolated a volatile alkaloid which they state is an optically active modification of β -methylpyrroline. Its hydrochloride showed an optical rotation at 21° C. of 2.77°.

Eberhardt³ isolated *dipentene*, Schimmel & Co.⁴ *phellandrene*, and Schreiner and Kremers⁵ *caryophyllene*.

Acids.—Arbenz⁶ reports 0.45 per cent of *oxalic acid* in pepper; Viehoveer, Kunke, and Mastin,⁷ however, found in sound Acheen pepper 1.61 per cent and in the product with more or less empty kernels 3.39 per cent.

Carbohydrates. Sugars.—Data on the kind and amount of sugars are lacking. Although soluble carbohydrates were not determined by Winton and co-workers,⁸ it may safely be assumed that these formed a considerable part of the undetermined matter and error in their analyses which averaged in decorticated white pepper 1.77, in white pepper 3.92, in black pepper 9.98, and in long pepper 15.55 per cent.

Starch is the chief constituent of pepper. The averages of analyses by Winton et al. (see table) show: decorticated white pepper 63.16, white pepper 56.47, black pepper 34.15, and long pepper 39.55 per cent. Whether the starch has ever been separated and purified, and its chemical and physical properties examined, does not appear.

Pentosans.—Hanus and Bien (see Introduction to Part III) found in black pepper 5.06, white pepper 2.20, and long pepper 3.75 per cent,

¹ Ber. 1907, 40, 3776.

² Helv. Chim. Acta 1927, 10, 593.

³ Arch. Pharm. 1887, 225, 575.

⁴ Schimmel & Co. Ber. Oct. 1890, 39.

⁵ Pharm. Arch. 1901, 4, 61.

⁶ Mitt. Lebensm. Hyg. 1917, 8, 98.

⁷ Science 1917, 46, 564.

⁸ Loc. cit.

dry basis. In a single variety of white pepper Böddener and Tollens¹ reported over 2 per cent of pentosans and 1.7 per cent of methylpentosans. Arragon,² by the Tollens furfurol-phloroglucinol method, found in white pepper 3.4 to 3.9 per cent, in black pepper 7.8 to 9.1, and in long pepper 6 per cent of pentosans (including methylpentosans?) dry basis. The figure obtained by subtraction of the pure from the crude starch represents largely pentosans. In the analyses made by Winton et al. the differences are: decorticated white pepper 1.69, average of all white peppers 2.70, average of all black pepper 4.48, and long pepper 3.33 per cent.

Mineral Constituents.—The analyses of the ash of 1 sample of black pepper made by Blyth,³ of 3 samples of black and 2 of white pepper made by Röttger,⁴ and of 1 sample of long pepper made by Hilger and Bauer⁵ are summarized below:

	K ₂ O	Na ₂ O	CaO	MgO	Fe ₂ O ₃	Mn ₂ O ₃	P ₂ O ₅	SO ₃	SiO ₂	Cl	CO ₂
	%	%	%	%	%	%	%	%	%	%	%
Black Pepper:											
Min.....	24.38	1.56	11.60	3.32	0.85	0.19	8.47	4.01	1.54	5.42	14.00
Max.....	34.72	5.51	16.07	13.00	2.16	0.89	11.10	9.61	6.53	8.46	20.11
Aver. (4)....	29.75	3.77	14.06	7.08	1.08	0.51*	10.03	5.43	4.01	7.02	17.64
White Pepper:											
Singapore....	7.15	0.84	31.06	11.65	1.86	0.21	30.75	3.76	1.46	0.91	10.02
	5.11	0.74	35.13	9.54	2.22	0.89	29.35	3.24	2.63	0.58	11.91
Long Pepper...	62.06†	13.97	4.08	2.19	8.36	3.02	10.00‡	9.05

* 2 samples. †KCl + NaCl. ‡ Includes sand.

LONG PEPPER

Piper officinarum DC. = *P. longum* Rumph. = *Chavica officinarum* Miq.

Fr. Poivre long. Sp. Pimienta larga. It. Peperone.
Ger. Langer Pfeffer.

Botanical and pharmaceutical authorities appear to agree that the above species yields the long pepper of commerce. It is a native of the Sunda and Philippine Islands and is grown chiefly in Java. An-

¹ J. Landw. 1910, 58, 229.

² Mitt. Lebensm. Hyg. 1915, 6, 160.

³ Foods, etc., London, 6th Ed. 1909, p. 495.

⁴ Arch. Hyg. 1886, 4, 183.

⁵ Forschungsab. Lebensm. 1896, 3, 113.

other species (*Piper longum* L. = *Chavica Roxburghii* Miq.), a native of India, the Philippines, and Timor, yielding compound fruits not exceeding 2 cm. in length, rarely enters commerce. Since both species have passed under the name of *P. longum* without the authority being given, some uncertainty exists as to the identity of the samples on which microscopical studies and chemical analyses have been reported.

Long pepper is an ingredient of whole mixed spices. English and American authorities have reported it as an adulterant of pepper, but importers and grinders strenuously deny that it could be successfully so used because of its higher cost.

MACROSCOPIC STRUCTURE (Fig. 74).—Highly characteristic is the elongated, cylindrical compound fruit (I), 5 to 8 mm. broad and up to 6 cm. long, with fruitlets (individual fruits) arranged in spirals, the whole suggesting an alder catkin. The *fruitlets* are completely grown together except for the exposed ends. As is shown in a cross section of the compound fruit (II), epicarp, hypoderm, and outer mesocarp are present only beneath the exposed surface.

MICROSCOPIC STRUCTURE.

Peduncle.—The *fiber* and *sclerenchyma* elements are like those of pepper, but *stone cells* appear to be few or lacking.

Pericarp.—The *epicarp* consists of polygonal cells and stomata much like those of pepper. *Stone cells* (Fig. 76, *st*) occur in the *hypoderm* but are arranged with their longer axis parallel to the surface, not perpendicular as in pepper. *Oleoresin cells* occur in the *outer mesocarp*.

A properly prepared tangential section (Fig. 75) of the compound fruit cut about midway from the surface to the axis will show two adjacent fruitlets in approximate cross section. Beginning with the tissues common to adjacent fruitlets, the layers are (1) *bundle zone* (*mes*²) or middle mesocarp with fibro-vascular bundles (*fv*) between two adjacent fruitlets, not in the angles; (2) *oil zone* (*mes*³) with large cells as in pepper containing oil drops; (3) reticulated *palisade cells* (*mes*⁴) corresponding to the porous cells of pepper; and (4) *endo-*

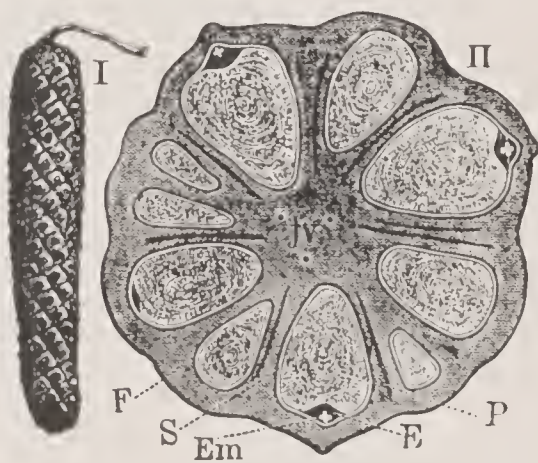


FIG. 74.—Long Pepper. I whole compound fruit. $\times 1$. II compound fruit in cross section showing fruitlets in longitudinal section: *F* pericarp with *fv* vascular bundles; *S* spermoderm; *P* perisperm; *E* endosperm; *Em* embryo. $\times 8$. (A.L.W.)

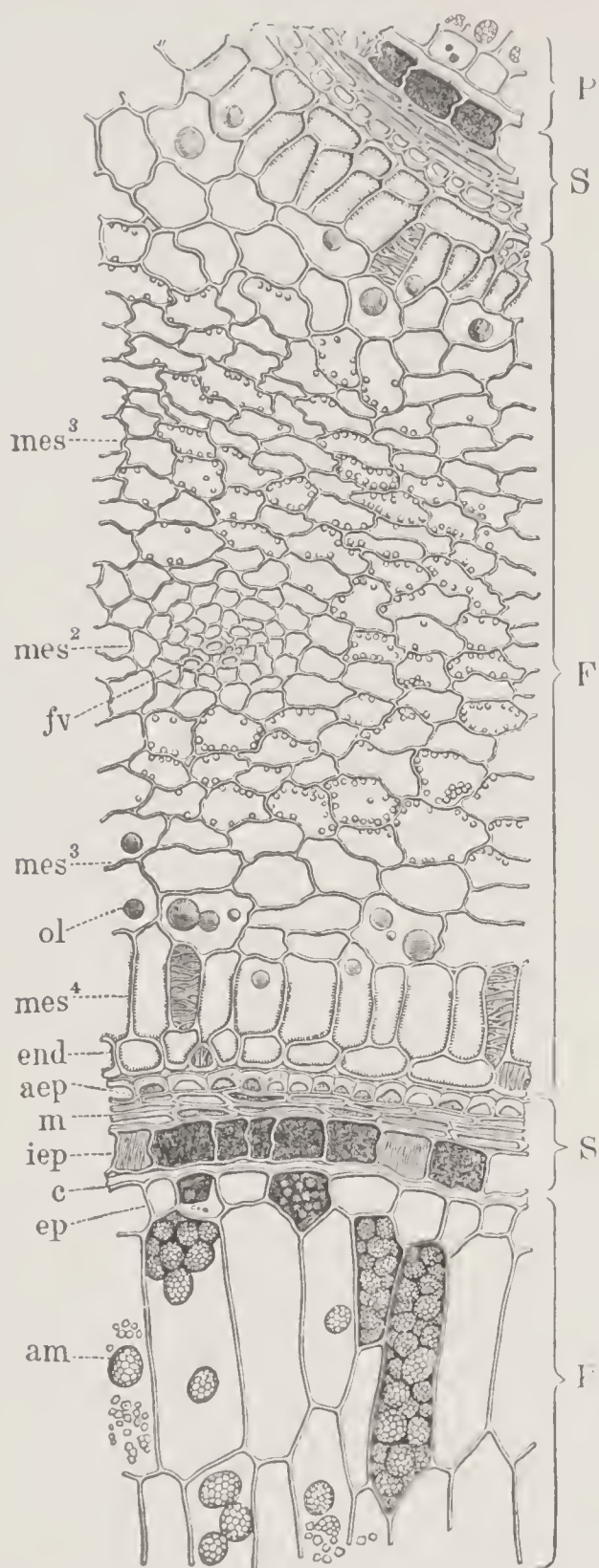


FIG. 75.—Long Pepper. Compound fruit in tangential section showing part of two fruitlets in cross section. *F* pericarp: *mes*² middle mesocarp with *fv* bundle; *mes*³ oily mesocarp with *ol* oil drops; *mes*⁴ reticulated mesocarp; *end* endocarp. *S* spermoderm: *aep* outer epidermis, *m* middle layers, *iep* inner epidermis. *P* perisperm: *ep* epidermis with *c* cuticle; *am* starch cells. $\times 160$. (A.L.W.)

carp (*end*) of longitudinally elongated cells with reticulations forming beads as seen in surface preparations, Fig. 76.

The reticulations on the *endocarp* are radial, while those on the *palisade cells* are tangential with reference to the fruitlet. In addition to the reticulations the inner walls and the inner radial walls of both layers show what in cross section appear to be numerous minute comb-like projections and in surface view fine pores.

Oil drops occur in the two inner layers as well as in the oil zone.

In both the first and second edition of Winton's *Microscopy of Vegetable Foods* and the second edition of Moeller's *Mikroskopie Nahrungs- u. Genussmittel* the occurrence of a thin layer with beaded, slightly undulating walls inside the endocarp is noted. More recent investigations have failed to disclose this layer. Possibly a thin layer of the wall of the ovary persists on parts of some fruits of both pepper and long pepper. Certainly such a layer occurs in cubebs between the endocarp stone cells and the spermoderm.

Spermoderm (Fig. 75, *S*; Fig. 76).—Corresponding with pepper, three layers are present, the *middle layer*, which on the body of the grain consists of one or more rows of cells (*m*), being absent or not evident at the apex.

The cell walls of the *outer epiderm* (*aep*; *aep*²) show a greater tendency to swell than those of pepper, the lumen, especially at the apex where the cells are small (*aep*¹), being much reduced in size.

Perisperm (Fig. 75, *P*).—Starch is usually present in the *outer epiderm* although protein predominates. Extending inward from the epiderm (*cp*), the cells are strongly elongated and contain *starch*

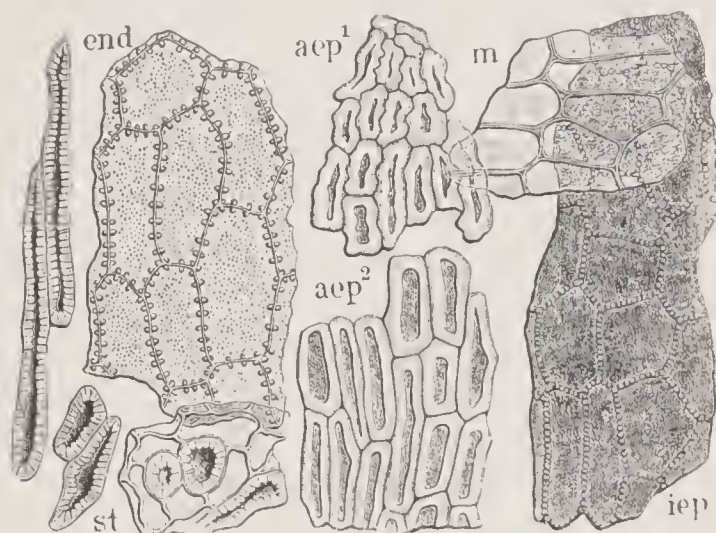


FIG. 76.—Long Pepper. Elements in surface view. *st* stone cells of hypoderm; *end* endocarp. Spermoderm: *aep*¹ and *aep*² outer epiderm at apex and on body of kernel; *m* middle layer; *iep* inner epiderm. $\times 160$. (A.L.W.)

grains (*am*) tending to larger size than those of pepper, the maximum reaching $10\ \mu$, although most of them do not exceed $6\ \mu$.

Oleoresin cells are not present.

Endosperm and **Embryo** are practically as in pepper.

CHIEF STRUCTURAL CHARACTERS.—Fruit compound, elongated; fruitlets in spirals.

Epicarp and hypoderm only at outer ends of fruitlets; hypoderm with transversely elongated stone cells; inner mesocarp of reticulated palisade cells; endocarp of elongated beaded cells (not beaker cells). Starch grains of perisperm up to $10\ \mu$. Perisperm without oleoresin cells.

CHEMICAL COMPOSITION.—See Pepper.

CUBEBS

Piper Cubeba L. fil. = *Cubeba officinalis* Miq.

Fr. Poivre cubèbe. Sp. Cubeba. It. Cubebe. Ger. Kubeben.

Although a drug and not recognized in the trade as a spice, cubebs are botanically closely related to pepper and exhausted cubebs are said at one time to have been used in fraudulent mixtures.

MACROSCOPIC STRUCTURE.—The *fruit* is distinguished from pepper by (1) the brown color, (2) the elongated base of the pericarp forming a stem, and (3) the loose *seed*.

MICROSCOPIC STRUCTURE.—The *endocarp* consists of large, uniformly thickened, often radially elongated stone cells. The cells of the *outer epiderm* of the spermoderm are much larger than those of pepper. The starch grains of the *perisperm* are also larger, reaching a maximum of 12 μ .

Further details are given in works on pharmacognosy.

CHEMICAL COMPOSITION.—No figures on the percentage of starch are available. Other constituents are nitrogenous substances, fixed and volatile oils, cubebic acid, fiber, and 5 to 9 per cent of ash.

Fixed Oil.—This consists of fatty oil, resins, and cubebin.

Cubebin, $C_{10}H_{10}O_3$ or $C_{20}H_{20}O_6$, first isolated by Soubeiran and Capitaine,¹ is a bitter crystalline substance melting at 125° C. Weidel² decomposed it into protocatechuic and acetic acids, and Pomeranz³ oxidized it to piperonylic acid. Its constitution and derivatives have been more recently studied by Mameli⁴ and Pauly, Schmidt, and Böhme.⁵

Volatile Oil.—The fruit contains 10 to 18 per cent of volatile oil.

The *Physical Values* follow: specific gravity at 15.5° C. 0.910 to 0.930, refractive index at 20° C. 1.493 to 1.498, and optical rotation −45 to −20°.

Constituents.—Ogliialoro⁶ identified *pinene* and *cubeb camphor*; Wallach⁷ isolated the sesquiterpene *cadinene* and another not identified. *Dipentene* is said to be present.

¹ J. Pharm. 1839, **25**, 355; 1840, **26**, 75.

² Jahresb. 1877, p. 68.

³ Wiener Sitzungsab. 1887 [2], **74**, 377.

⁴ Gaz. chim. ital. 1921, **51**, II, 353.

⁵ Ber. 1924, **57B**, 1327.

⁶ Gaz. chim. ital. 1875, **5**, 467.

⁷ Ann. 1887, **238**, 78.

FRUITS OF THE MAGNOLIA FAMILY

(*Magnoliaceæ*)

Most members of the family furnish valuable wood for timber, and some produce bark, fruit, or seeds containing aromatic bitter resins employed as drugs and incense; star anise is the only important species classed as a food plant.

STAR ANISE

Illicium verum Hook. f.

Fr. Anis étoilé. Sp. Anis estrellado. It. Badiano. Ger. Sternanis.

The star-shaped cluster of fruits with the odor and flavor of anise furnish a spice much used in the Orient. Formerly the species was thought to be *I. anisatum*, but it is now known that *I. anisatum* L. and *I. religiosum* Sieb. are synonyms for shikimi, the poisonous fruit of a tree often grown about Buddhist temples.

MACROSCOPIC STRUCTURE.—The 6 to 8 (rarely 9 to 12) dark brown carpels form a flat expanded rosette radiating from the tip of a slender stem. Each laterally flattened, pointed, boat-shaped *carpel*, bearing a single seed, is 12 to 20 mm. long, 8 to 10 mm. high, and dehiscent on the upper side. Each of the lustrous, light brown, obovoid, anatropous *seeds*, 5 to 8 mm. long, contains a bulky endosperm and minute embryo.

MICROSCOPIC STRUCTURE. **Stem.**—Among the otherwise normal stem tissues are the characteristically branched stone cells called "astroscelereids" by Tschirch.

Pericarp.—This is made up of (1) *epicarp* of large, wavy-walled, porous cells, with much-thickened outer walls, strikingly striated cuticle, and stomata; (2) *mesocarp* of thin-walled, small cells with brown contents, oleoresin cells, branching stone cells, similar to those of the stem, fibro-vascular bundles, and, adjoining the endocarp on the dehiscence surface, a mass of sclerenchyma fibers about 500 μ

thick; and (3) *endocarp* of sclerenchymatized but thin-walled palisade cells up to 600 μ high and 60 μ broad, passing into short stone cells at the point of dehiscence.

Vogl calls attention to the cuticularized walls of the oleoresin cells which stain an intense red with alcoholic fuchsin.

Spermoderm.—Characteristic are (1) *outer epiderm* of thick-walled, sclerenchymatized palisade cells 150 to 200 μ high and 30 to 70 μ broad, forming a yellow, brittle layer easily breaking away from the underlying tissues; (2) *subepiderm* of large, often longitudinally elongated, thick-walled, sclerenchymatized cells, loosely arranged; (3) thin-walled *spongy parenchyma*; and (4) *compressed cells* containing large prismatic calcium oxalate crystals.

Endosperm.—Thin-walled cells containing fat and aleurone grains.

Embryo.—Characterless tissues.

CHIEF STRUCTURAL CHARACTERS.—Carpels boat-shaped, forming rosettes. Seeds anatropous. Endosperm bulky; embryo minute.

Pericarp with striated cuticle of epicarp, branching stone cells of mesocarp, and endocarp of palisade cells. Spermoderm with outer epiderm of thick-walled palisade cells. Endocarp cells thin-walled, containing fat and aleurone grains.

CHEMICAL COMPOSITION.—True star anise and the poisonous shikimi, according to Arnst and Hart,¹ contain:

COMPOSITION OF STAR ANISE AND SHIKIMI (ARNST AND HART)

	Water	Protein	Oil, fixed	Oil, volatile	N-f. ext.	Fiber	Ash
	%	%	%	%	%	%	%
Star anise	13.16	5.15	5.85	4.79	37.51	30.89	2.65
Shikimi	11.94	6.35	2.35	0.66	48.01	27.91	11.94

The *U. S. Standards* limit the percentage of total ash in star anise to 5 per cent and require that star anise extract contain at least 3 per cent of star anise oil.

Fixed Oil.—Bulir² gives the following values and percentages of fatty acids in the fixed oil of star anise and shikimi:

¹ Z. angew. Chem. 1893, 6, 136.

² Z. Unters. Nahr.-Genussm. 1912, 24, 309.

	Sp. gr. 15° C.	Iodine No.	Stearic acid	Palmitic acid	Oleic acid	Linolic acid
			%	%	%	%
Star anise (yield 20%) . . .	0.9264	93.1	2.6	23.2	45.0	23.9
Shikimi (yield 12.5%) . . .	0.9295	90.6	2.5	22.5	60.2	9.8

Volatile Oil.—By Von Fellenberg's chromic acid oxidation method, Zäch¹ obtained 8 to 12 per cent. The maximum usually given is 5.

Physical and Chemical Values.—The values of anise and star anise oils appear to vary within practically the same limits, the only marked difference noted being that star anise oil may have a stronger minus polarization, reaching in some instances -12° . Values reported for shikimi oil also fall within the same limits. Seaber and Marshall² consider that the minimum of 1.5520 at 25° C. for refractive index of star anise oil given by some authors is too high.

Constituents.—*Anethole*, *methyl chavicol*, and *anise-ketone* occur in star anise oil as well as in anise oil (which see). Chiris³ confirms Tardy⁴ as to the presence of aniseketone. *Safrole* was found by Oswald.⁵ Other constituents present in star anise oil, according to Schimmel & Co.,⁶ are *cineol*, *p-cymol*, α -*terpineol*, *methyl chavicol*, *p-cymene*, *l- α -* and β -*phellandrene*, *d- α -pinene*, *dipentene*, *l-limonene*, and *hydroquinone ethyl ester*.

Schimmel & Co.⁷ observe that shikimi oil contains much safrole but little anethole, whereas star anise oil contains much anethole and but little safrole.

Acids and Toxic Substances.—In shikimi, Eykmann,⁸ in addition to *shikimol* (safrole) and a terpene, *shikimene* ($C_{10}H_{16}$), found three acids, namely: *protocatechouic acid* ($C_6H_3(OH)_2(COOH)$), *shikimic acid* ($C_6H_2(OH)_3(COOH)$), and another acid not identified; also *shikimin* ($C_7H_{10}O_5$), believed to be toxic, and *shikimipicrin* ($C_7H_{10}O_3$ or $C_{10}H_{14}O_4$).

¹ Mitt. Lebensm. Hyg. 1932, **23**, 156.

² Perf. Ess. Oil Rec. 1931, **22**, 163.

³ Parf. France 1926, **38**, 119.

⁴ Thesis, Paris, 1902.

⁵ Arch. Pharm. 1891, **229**, 86.

⁶ Schimmel & Co. Rep. Apr. 1893, 61; Oct. 1895, 7; Apr. 1910, 99, 100; Oct 1911, 86.

⁷ Ibid. Apr. 1909, 57.

⁸ Rec. trav. chim. Pays-Bas 1885, **4**, 32.

Of this formidable array, Siersch¹ identified, in both star anise and shikimi, shikimic acid in crystalline form, the latter containing much more than the former, and also isolated, from shikimi, crystals in minute amount of a substance corresponding to shikimi and of an unidentified substance. Both fruits contained saponin. This author, even if not able to clarify the situation fully, has at least performed a good service in correcting various errors which have passed from one author to another.

Pentosans.—In the dry matter, true star anise 13.79 and Japanese star anise 11.37 per cent. See Hanus and Bien in Introduction to Part III.

¹ Pharm. Zentralh. 1928, 69, 581.

SEEDS OF THE NUTMEG FAMILY

(*Myristicaceæ*)

NUTMEGS and mace are products of the species described below.

MACE

Myristica fragrans Hout.; *M. argentea* Warb.; *M. malabarica* Lam.

Fr. Macis. Sp. Macis. It. Macia. Ger. Macis.

Unless otherwise stated mace is the aril and nutmeg (which see) is the seed kernel of the first species, a native of the Banda Islands and probably neighboring regions, but widely cultivated in the East Indies, also to some extent in the Malay Peninsula, Madagascar, Réunion, the West Indies, and South America.

Macassar or Papua mace and nutmeg, products of *M. argentea* Warb., are inferior. Bombay mace, the aril of *M. malabarica* Lam., is a nearly tasteless and odorless adulterant.

MACROSCOPIC STRUCTURE.—The nutmeg *tree* is dioecious, but by grafting male scions on female trees fertilization is effected. The *flowers* have a three-lobed calyx, hairy on the outer surface. By the union of the anthers the stamens form a column. The female flower has a one-celled, one-ovuled ovary, developing into the fleshy peach-like nutmeg fruit (which see).

On ripening, the *fruit* splits in half disclosing the bright red *aril* tightly grasping with its flattened and branching arms the anatropous *seed* (Fig. 77, I). The lustrous dark brown shell (spermoderm and outer perisperm) bears on its surface depressions formed by the pressure of the arms of the aril. Raphe and chalaza are also evident. On the shell being cracked the nutmeg is liberated.

Banda or True Mace (Fig. 77, I) is of a light buff color, the bright red color having disappeared in curing. Penang is one of the best commercial grades, Batavia one of the poorest.

Macassar Mace (Fig. 77, IV) has broader arms than Banda mace and dries to a dirty brown color. It has a wintergreenlike flavor.

Bombay Mace (Fig. 77, III) has numerous narrow arms dividing

at the apex into a confused mass of narrow, curling branches, the whole being about twice as long as Banda mace.

MICROSCOPIC STRUCTURE (Figs. 78, 79, 80, and 81).—All three varieties of mace have the same general structure: (1) *outer epiderm* (*ep*) of longitudinally much elongated cells with somewhat thickened walls and a cuticle (*c*); (2) *hypoderm* (*hy*) of cells with walls differing in thickness according to the variety; (3) *mesophyl* of more or less isodiametric cells containing amyloextrin-starch (*ads*),



FIG. 77.—Mace and Nutmegs. I Banda mace clasp. II Banda nutmeg. III Bombay mace. IV Macassar mace. V Macassar nutmeg. $\times 1$. (A.L.W.)

large oleoresin cells (*ol*), and fibro-vascular bundles (*fv*); and (4) *inner epiderm* similar to the outer.

The *epiderm* cells and their lumens are broadest in Banda mace, the average width of the cells being about $25\ \mu$, whereas in Bombay mace it is about half that figure and in Macassar mace about two-thirds. Owing to the thickening of the walls, the lumen is much reduced in Macassar and Bombay mace. A distinct radial elongation of the cells is characteristic of Bombay mace.

A *hypoderm* with cells smaller and thicker-walled than those of the mesophyl is marked in Banda and Macassar mace, but is not noticeably differentiated in Bombay mace.

The *amylodextrin-starch grains* (so named by Tschirch) differ from starch grains in that they give a red or brown color with iodine in potassium iodide. Attention has been called by several authors to the elongated, often bone-shaped forms which separate from the masses on mounting. These we find are compound, their shape depending on the arrangement and shape of individual grains which differ little from ordinary starch grains. The end members of a rod-

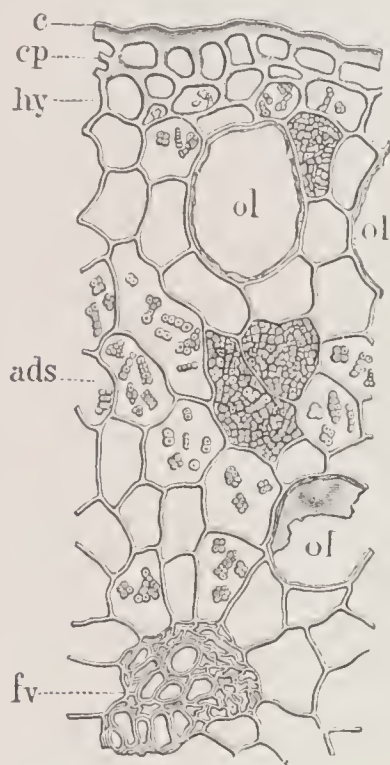


FIG. 78.

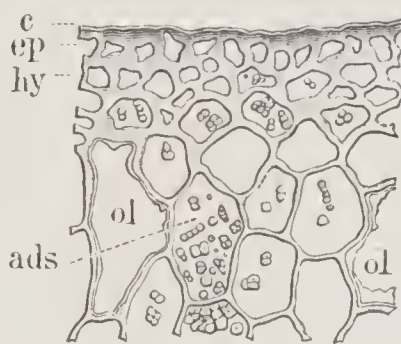


FIG. 79.

FIG. 78.—Banda Mace. Outer half in cross section. *cp* epiderm with *c* cuticle; *hy* hypoderm; mesophyl with *ads* amyloidextrin-starch cells, *ol* oleoresin cells, and *fv* bundle. $\times 160$. (A.L.W.)

FIG. 79.—Macassar Mace. Outer layers in cross section. *cp* epiderm with *c* cuticle; *hy* hypoderm; mesophyl with *ads* amyloidextrin-starch cells and *ol* oleoresin cells. $\times 160$. (A.L.W.)

shaped aggregate are plano-convex, the middle members quadrilateral, often nearly square. A distinct hilum is visible in each individual grain, especially in mounts treated with alcohol and ether. This treatment also helps bring out the dividing lines between members of an aggregate. The maximum size of the individual grains is largest in Macassar mace (about $7\ \mu$), smallest in Bombay mace ($4\ \mu$), intermediate in Banda mace (5 to $6\ \mu$).

CHIEF STRUCTURAL CHARACTERS.—Macroscopic characters: see Fig. 77.



FIG. 80

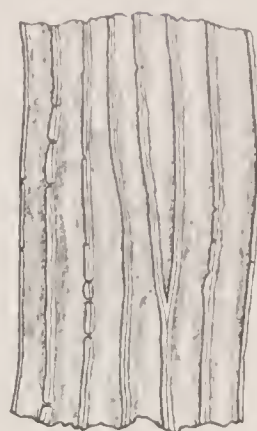


FIG. 81.

FIG. 80.—Bombay Mace. Outer layers in cross section. *ep* epiderm with *c* cuticle; *hy* hypoderm; mesophyl with *ads* amylodextrin-starch cells and *ol* oleoresin cells. $\times 160$. (A.L.W.)

FIG. 81.—Banda Mace. Epiderm in surface view. $\times 160$. (A.L.W.)

Microscopic characters are summarized in the following table:

	Banda	Macassar	Bombay
Epiderm cells, average breadth.....	25 μ	17 μ	13 μ
“ “ lumen.....	large	narrow	narrow *
Hypoderm walls.....	thick	thick	thin
Amylodextrin-starch grains, max.....	6 μ	7 μ	4 μ
Oleoresin, direct.....	yellow	yellow	orange
“ with alkali.....	“	“	red

* Radially elongated.

MICROSCOPY OF MACE PRODUCTS. **Ground Mace.**—Of great value in diagnosis of ground mace are the contents of the oleoresin cells which are of a deep orange color in Bombay mace and become red with sodium hydroxide, whereas in the other two varieties the color is yellow even after the addition of the alkali.

CHEMICAL COMPOSITION.—See Nutmeg.

NUTMEG

Myristica fragrans Hout.; *M. argentea* Warb.; *M. malabarica* Lam.

Fr. Noix muscade. Sp. Nuez moscada. It. Noce moscada.
Ger. Muskatnuss.

Under mace are given the nomenclature and geographical distribution of species yielding nutmeg and mace.

MACROSCOPIC STRUCTURE.—True or Banda Nutmegs (Fig. 77, II) are ovoid, slightly longer than broad, with a wrinkled surface and a shallow longitudinal depression formed by the pressure of the raphe during growth.

• **Macassar or Long Nutmegs** (Fig. 77, V) are about twice as long as broad.

Both varieties come into the market unlimed (brown nutmegs) or limed; the latter, owing to soaking in lime water, have a white coating which is especially marked in the furrows. Among the best known commercial varieties of Banda nutmegs are Penang, Singapore, Padang, and West Indian.

A cross section shows dark streaks of perisperm and light streaks of endosperm. On pressing the dark streaks oil exudes. The small embryo, located beneath the micropyle at the base of the nutmeg, has cotyledons with long, narrow branches, extending into the surrounding tissues, which conduct the reserve material to the plantlet during sprouting.

MICROSCOPIC STRUCTURE.—Berg in his Atlas (1865) shows all the seed tissues including shell in cross section, but he mistook the perisperm for inner spermoderm, an error generally accepted until Voigt¹ by developmental studies disclosed its true nature. Hallström² in his studies of the comparative anatomy of the group brought out other characters, particularly that the fiber layer within the inner palisade layer belongs to the perisperm and is present in nutmegs of all the common species except Macassar.

The shell consists of the thick spermoderm together with a portion of the perisperm.

Spermoderm.—Four layers of the shell are classed as spermoderm: (1) *outer epiderm* of polygonal cells and stomata, (2) *parenchyma* with raphe system, (3) *outer palisade layer* of thin-walled cells between 100 and 200 μ high, and (4) *inner palisade layer* of scleren-

¹ Ann. Jar. Bot. Buitenzorg. 1888, 7, 151.

² Arch. Pharm. 1895, 233, 441.

chyma cells, up to 1 mm. high, containing here and there a crystal of calcium oxalate.

Perisperm (Fig. 82).—This consists of three layers of distinct tissues, separation of the nutmeg taking place through the second: (1) longitudinally elongated *fibers* in a single interrupted layer, (2) *primary perisperm* (PN) of tangentially elongated sclerenchyma cells containing crystals (*cr*), and (3) *secondary perisperm* (SN) of isodiametric cells, fibro-vascular bundles (*fv*), and, especially in the dark arms penetrating the endosperm, numerous oleoresin cells (*ol*).

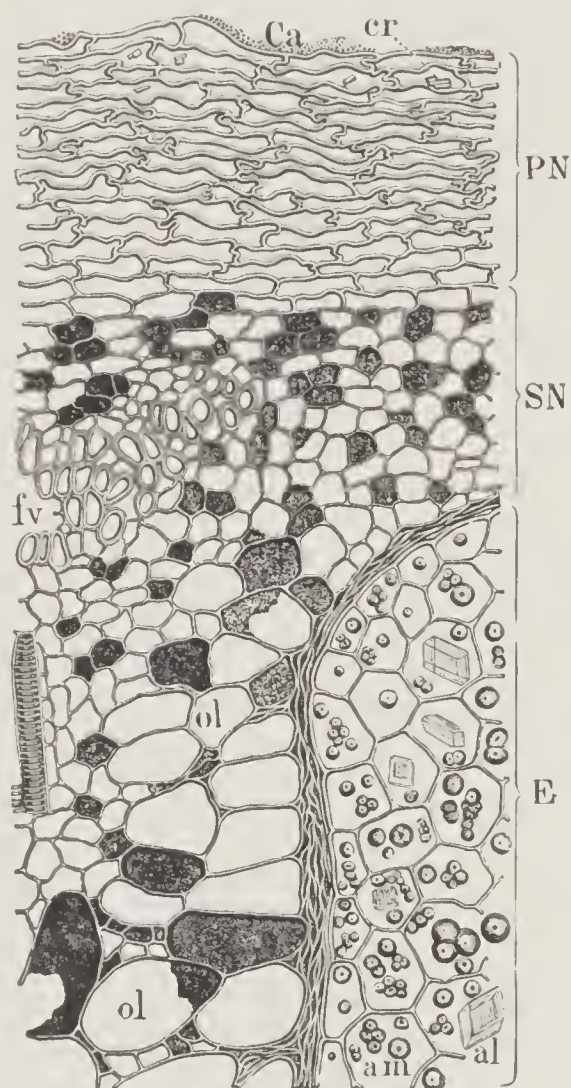


FIG. 82.—Banda Nutmeg. Cross section. *Ca* coating of calcium carbonate. *PN* primary perisperm containing *cr* crystals. *SN* secondary perisperm: *fv* bundle; *ol* oleoresin cells. *E* endosperm: *am* starch grains; *al* crystalloid. $\times 160$. (A.L.W.)

The crystals in the primary perisperm, according to Tschirch and Oesterle¹ have the properties of potassium tartrate. Finely divided calcium carbonate (*Ca*) occurs on the surface of limed nutmegs.

Endosperm (Fig. 82, *E*).—Compressed cells, belonging according to Voigt² with the endosperm, separate the secondary perisperm from the active endosperm. The latter consists of polygonal cells containing starch grains (*am*) and beautiful aleurone crystalloids (*al*).

The *starch grains* are round or truncated, with a distinct central hilum, and occur often in aggregates of two or more individuals. They show distinct polarization crosses.

Strikingly different are the *crystalloids* which are not affected by polarized light. A matrix of ground substance is not ordinarily visible.

Embryo.—Usually disorganized in commercial nutmegs.

CHIEF STRUCTURAL CHARACTERS.—Nutmeg wrinkled, in section with dark (secondary perisperm) and light (endosperm) streaks.

¹ Anat. Atlas, Leipzig, 1900, p. 250.

² Loc. cit.

Primary perisperm of tangentially elongated cells containing tartrate crystals; secondary perisperm of polygonal cells, oleoresin cells, and fibro-vascular bundles. Endosperm with starch grains and crystalloids.

CHEMICAL COMPOSITION.—The analyses of nutmeg and mace by Winton, Ogden, and Mitchell¹ given below were all from original packages. The Singapore, Padang, and Macassar nutmegs were limed, which increased somewhat the percentage of total ash. The Penang nutmegs were unlimed or "brown"; their size is indicated by the designation 54's and 80's, which refer to the number per pound of 454 grams. Analyses of the worm-eaten nutmegs show that the insects had devoured starch and fixed oil, thus increasing the volatile oil. Macassar, or long nutmegs, differ little in composition from true nutmegs. Of special interest are the high percentages of fixed oil (non-volatile ether extract) and "starch" (amylodextrin starch) in mace and Bombay mace. The somewhat lower content of volatile oil in these two kinds does not fully show their inferiority since the flavor of Macassar mace is rank, suggesting wintergreen, and that of Bombay mace is not aromatic.

The volatile oil of West Indian nutmeg and mace, according to Clevenger,² is lower in specific gravity and refractive index, but higher in plus polarization, than the East Indian products. The nutmegs of all regions yield a volatile oil with a higher polarization than that of the corresponding mace, due it is believed to a loss of the more volatile constituents of the latter. Clevenger's results show that shriveled nutmegs are richer in volatile oil than the sound mature ones, thus confirming the results given in the table on the next page.

The *U. S. Standards* permit a thin coating of lime on nutmeg (*Myristica fragrans*), but require that it contain not less than 25 per cent of non-volatile ether extract, not more than 10 per cent of fiber, 5 per cent of total ash, nor 0.5 per cent of sand. They further require that mace (*Myristica fragrans*) contain not less than 20 per cent nor more than 30 per cent of non-volatile ether extract, not more than 10 per cent of fiber, 3 per cent of total ash, nor 0.5 per cent of sand.

Fixed Oil.—Nutmeg butter has long been prepared on a small scale in the East Indies from damaged and inferior nutmegs. The ground spice is either steamed and pressed or pressed hot without steaming. Although consisting largely of fatty oil, volatile oil varying up to 10 per cent is present, which fact together with the variable quality

¹ Connecticut Agr. Exp. Sta. Rep. 1898, p. 184; 1899, p. 100.

² J. Ass. Off. Agr. Chem. 1935, 18, 611.

COMPOSITION OF NUTMEG AND MACE (WINTON, OGDEN, AND MITCHELL)

	Water	Pro- tein	Oil, fixed	Oil, vola- tile *	Alcohol extract	Starch, pure†	Starch, crude‡	Fiber	Ash, total	Ash, solu- ble	Sand
	%	%	%	%	%	%	%	%	%	%	%
<i>Nutmegs</i>											
Singapore:											
Min.....	5.79	6.56	36.29	2.56	10.42	23.34	25.51	2.38	2.13	0.82	0.00
Max.....	8.98	7.00	36.94	3.40	11.09	24.20	25.60	2.65	2.48	0.93	0.01
Aver. (3)	7.63	6.73	36.70	3.02	10.77	23.72	25.56	2.51	2.28	0.86	0.00
Penang:											
54's.....	7.69	6.19	31.26	5.03	10.49	30.09	2.40	1.85	0.85	0.04
80's.....	9.40	7.12	34.80	2.64	11.71	26.16	2.70	1.88	0.76	0.00
Padang....	10.83	6.75	28.73	6.94	17.38	14.62	17.19	3.72	3.26	1.46	0.00
Worm-eaten	17.23	9.73	11.32	9.76	14.71	1.63	5.71	7.95	6.37	4.33	0.12
Macassar..	5.24	6.95	32.88	4.70	16.79	29.25	29.97	2.07	3.32	1.25	0.00
<i>Mace</i>											
Banda:											
I.....	10.75	6.25	22.00	8.65	23.05	27.90	32.35	3.04	1.81	1.09	0.00
II.....	7.82	6.81	23.82	10.80	27.02	27.17	3.10	1.74	1.00	0.00
Penang:											
Min.....	9.41	6.06	21.23	6.27	22.07	23.12	26.77	2.94	1.67	0.92	0.03
Max.....	12.04	7.00	23.72	8.65	26.04	31.61	34.42	3.85	2.54	1.33	0.21
Aver. (4)	10.71	6.42	22.29	7.59	23.86	28.80	31.53	3.25	1.98	1.09	0.08
Batavia...	8.89	7.87	22.00	13.03	27.07	22.68	4.01	2.49	1.26	0.21
Damaged..	12.51	10.94	20.96	14.97	22.27	4.73	8.32	7.64	5.74	2.37	1.13
Macassar..	4.18	7.00	53.54	5.89	32.89	8.78	10.39	4.57	2.01	1.11	0.03
Bombay...	0.32	5.06	59.81	4.65	44.27	14.51	16.20	3.21	1.98	1.37	0.07

* Volatile ether extract. † Diastase method. ‡ Reducing matter, after washing with 10% alcohol and direct inversion of residue, calculated as starch.

of the raw material and the primitive method of manufacture explains the wide range in composition.

The Physical and Chemical Values, as given by different authors, vary within the following limits:

	Sp. gr. 15° C.	Ref. ind. 40° C.	Melting point	Saponi- fication No.	Iodine No.	Reichert- Meissl No.	Fatty acids titer
			°C.				°C.
Min.....	0.945	1.4665	38	153	40	1.0	35
Max.....	0.996	1.4704	52	200	86	4.2	45

Values of nutmeg fat, recently obtained by Heiduschka and Häbel,¹ follow: specific gravity at 15° C. 0.9779, melting point 42° C., refractive index at 40° C. 1.4704, optical rotation at 40° C. +67.05°.

¹ Arch. Pharm. 1933, 271, 56.

Constituents of Fixed Oil.—Power and Salway¹ determined the constituents of nutmeg butter as expressed in the laboratory. The ether extract of the nutmegs used was 42.9 per cent; the yield of expressed butter was 26.6 per cent. By removal of the volatile oil in a current of steam, the weight of the butter was diminished by 12.5 per cent and the iodine number from 57.8 to 35.7. The values of the volatile oil thus removed were: specific gravity 20°/20° 0.8794 and optical rotation +22.5°.

The constituents identified and their estimated amounts, as calculated free from the volatile oil by Power and Salway, follow: volatile oil 0.0; *trimyristin* 83.4; *olein* or *oleic acid* 3.4; *linolenic acid* as glyceride 0.6; resins 2.3; unsaponifiable matter (includes *myristicin*, *phytosterol*, and a new compound, $C_{18}H_{22}O_5$) 9.7; and undetermined by difference (includes formic, acetic, and cerotic acids) 0.6 per cent.

Collin and Hilditch² give the following analysis of the mixed fatty acids: lauric acid 1.5, myristic acid 76.6, palmitic acid 10.1, oleic acid 10.5, and linolic acid 1.3 per cent.

The composition of the nutmeg fat, calculated by Heiduschka and Häbel from the values credited to them above, follow: volatile oil 2.4, trimyristin 59.5, tripalmitin 5.0, triolein 8.5, free myristic acid 9.0, free palmitic acid 6.2, and unsaponifiable matter 9.4 per cent.

The composition of the fatty acids of the fat of Bombay mace, as given by Collin and Hilditch,² follows: myristic acid 39.2, palmitic acid 13.3, other saturated acids 2.4, oleic acid 44.1, and linolic acid 1.0 per cent.

Trimyristin or *myristin*, $C_3H_5(O \cdot C_{14}H_{27}O)_3$, is the triglyceride of myristic acid ($C_{13}H_{27}COOH$) of the $C_nH_{2n}O_2$ series. It is the chief constituent of the fixed oils of nuts of species of *Myristica* and occurs in small amounts in various animal fats. From an ether solution it crystallizes in laminæ melting at about 56° C. which may be converted, by heating beyond the melting point and cooling, into an opalescent mass with a lower melting point. See Thoms and Mannich.³

Macilenic Acid, $CH_3(CH_2)_5CH : CH(CH_2)_5COOH$.—From the petroleum ether extract of mace, on freezing, Tschirch and Schklowsky⁴ separated as needles melting at 70° C. this monocarboxylic acid belonging to the oleic series ($C_nH_{2n-2}O_2$). The authors state that they are the first to separate this acid from vegetable material. Lewko-

¹ J. Chem. Soc. 1908 93, 1653.

² J. Soc. Chem. Ind. 1930, 49, 141T.

³ Ber. deut. pharm. Ges. 1901, p. 264.

⁴ Arch. Pharm. 1915, 253, 102.

witsch¹ lists a corresponding acid but without a name. Since the authors were unable to isolate glycerin in the petroleum ether extract, they conclude that the acid exists free.

On distilling *in vacuo* the petroleum ether extract, after separation of the macilenic acid, *macilolic acid*, a hydroxycarboxylic acid, was separated from the highest-boiling-point fraction in the form of scales melting at 68° C.

From the chloroform extract, crystals of a *phytosterol*, melting at 131° C., were obtained.

Volatile Oil of Nutmeg and Mace.—Although nutmeg and mace oils are often regarded as identical in composition and properties, such is not strictly the case. Both are colorless with the fragrance of the spices. By Von Fellenberg's chromic acid oxidation method Zäch² obtained 3 to 8 per cent in nutmeg and 5 to 14 in mace.

Physical and Chemical Values.—The range for nutmeg oil follows:

	Sp. gr. 15.5° C.	Ref. ind. 20° C.	Opt. rot. 25° C.	Ester No.	Acetyl No.*	Acid No.	Sol. 90% alcohol
Min.....	0.865	1.476	+ 8	2	25	0.5	vols. 0.5
Max.....	0.930	1.488	+40	9	31	3.0	3.0

* Ester number after acetylation.

The chemical values in the table are those given by Gildemeister and Hoffmann.³ As prepared by Power and Salway and used in their studies noted below, nutmeg oil had the following values: specific gravity at 15° C. 0.869, rotation +38.06, ester number 3.15, and acid number 0.81.

As given by Gildemeister and Hoffmann the values of mace oil are as follows: specific gravity at 15° C. 0.890 to 0.930, optical rotation +10 to +22, and soluble in 2 to 3 volumes of 90 per cent alcohol.

Constituents of Nutmeg and Mace Oil.—Passing over the pioneer work of Wallach⁴ and Wright,⁵ Thoms⁶ gives the following constituents of mace oil: *pinene*, *dipentene*, *myristicol*, *myristicin*, *myristic acid*, and *phenols*.

¹ Chem. Technol. Anal. Oils, etc., London, 1913, 1, 111.

² Mitt. Lebensm. Hyg, 1932, 23, 156.

³ Ätherischen Öle, Leipzig, 3 Aufl. 1929, 2, 596.

⁴ Ann. 1885, 227, 288; 1889, 252, 105.

⁵ J. Chem. Soc. 1873, 26, 549.

⁶ Real.-Enzykl. ges. Pharm.; Berlin, 1907, 9, 548.

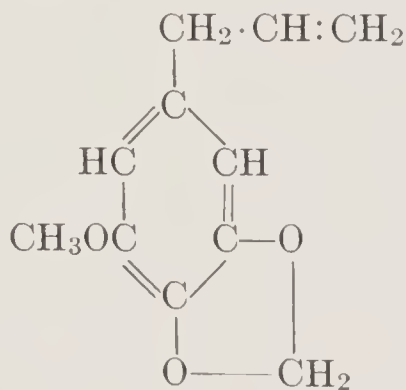
Power and Salway¹ add several substances to the foregoing list and give the following approximate quantitative results obtained on Ceylon nutmeg oil:

	%
<i>d</i> -Pinene and <i>d</i> -camphene.....	80.0
Dipentene.....	8.0
Eugenol and isoeugenol.....	0.2
<i>d</i> -Linaloöl, <i>d</i> -borneol, <i>i</i> -terpineol and geraniol.....	6.0
Safrole.....	0.6
Myristicin.....	4.0
Free myristic acid and esters.....	0.3
Esters of formic, acetic, butyric, and octoic acids, etc.	0.9
	<hr/> 100.0

The authors also found traces of a new alcohol, yielding on oxidation a diketone ($C_8H_{14}O_2$), a new *monocarboxylic acid* ($C_{13}H_{18}O_3$), and an *aldehyde* resembling citral but having a β -naphthocinchoninic acid derivative.

Schimmel & Co.,² in nutmeg oil with values falling within the limits given above, found 70 per cent of *terpenes* and 7 to 10 per cent of *alcohols*. The fraction boiling at 156 to 159°, amounting to 30 per cent, consisted mostly of *pinene* and *camphene*. The 159 to 180° fraction formed 39 per cent; it contained α -*pinene*, β -*pinene*, *p*-*cymene* (melting point 155 to 156°). Dipentene was not obtained pure. In the 205 to 225° fraction were *d*-*linaloöl*, *geraniol*, *d*-*terpineol*, and α -*terpineol*.

Myristicin, $C_{11}H_{12}O_3$.—This constituent of nutmeg occurs both in the volatile and fixed oils. As a result of the studies of Semmler³ and Thoms⁴ its structural formula has been established as shown herewith:



Myristicin

¹ J. Chem. Soc. 1907, 91-2, 2037.

² Rep. Apr. 1910, 80.

³ Ber. 1890, 23, 1803; 1891, 24, 3818.

⁴ Ibid. 1903, 36, 3446; Arb. Pharm. Inst. Berlin 1904, I, 18, 23.

It is an oily substance boiling at 155° C. under pressure of 17 mm. The narcotic principle of nutmegs appears to be myristicin. Physiological tests by Dale, supplementing the work of Power and Salway¹ on the constituents, support this view.

d-Pinene, $C_{10}H_{16}$, a common bicyclic terpene, is the chief constituent of turpentine and many volatile oils. It is a liquid; specific gravity at 20° C. 0.859, boiling point 156° C.

d-Camphene, $C_{10}H_{16}$, also a bicyclic terpene, is a solid melting at 48° C. and boiling at 160° C. It occurs also in ginger oil.

Dipentene, $C_{10}H_{16}$, also known as inactive (*i*) limonene, a monocyclic terpene, is a colorless liquid; specific gravity at 20° C. 0.845, boiling point 175 to 176° C. It occurs in many volatile oils.

Carbohydrates. *Amylodextrin Starch*, $6(C_6H_{10}O_5) \cdot 2H_2O$.—Tschirch and Schklowsky² found that, in both hot and cold water extracts of mace, amylodextrin starch was present and was precipitated by alcohol.

Pentosans.—Hanus and Bien found in nutmeg 2.48, in mace 4.39 per cent dry basis. See Introduction to Part III.

Colors.—A red-yellow coloring substance, with a spectrum similar to that of *xanthophyl*, was isolated by Tschirch and Schklowsky.²

¹ Am. J. Pharm. 1908, 80, 563.

² Loc. cit.

FRUITS OF THE LAUREL FAMILY

(*Lauraceæ*)

THE species yielding cassia buds described herewith is believed to be the same as that which yields cassia bark.

CASSIA BUDS

Cinnamomum Cassia Bl.

Fr. Fleurs de cannellier. Sp. Flores de casia. It. Fiori del cinnamone del Malabar. Ger. Zimtblüten.

The English name "cassia buds" is a misnomer as is also "cassia flowers"—the literal translation of the names used in several European languages—since the product is neither a bud nor a flower, but an immature fruit enclosed within the persistent calyx. There appears to be some doubt whether the buds are produced by the same tree as that yielding China cassia (which see)—at least all the works on food or drugs published during the past half century that the writers have consulted follow one the other in stating that such is "probably" the case.

MACROSCOPIC STRUCTURE.—Short, slender *pedicels* or stems (less than 10 mm.) often remain attached to individual buds, and occasionally the stem from which these pedicels fork is also present.

The *fruit* is surrounded and entirely covered, except for the brown, dome-shaped top, by the black, thick, woody, urn-shaped *calyx*, the whole resembling a miniature acorn flush with or slightly protruding from the cup. The similarity is further heightened by the roughened calyx and the smooth, lustrous pericarp with the nipplelike base of the style in the center of the top. The calyx is usually 7 to 10 mm. long, about half being the narrow tube which expands rather abruptly

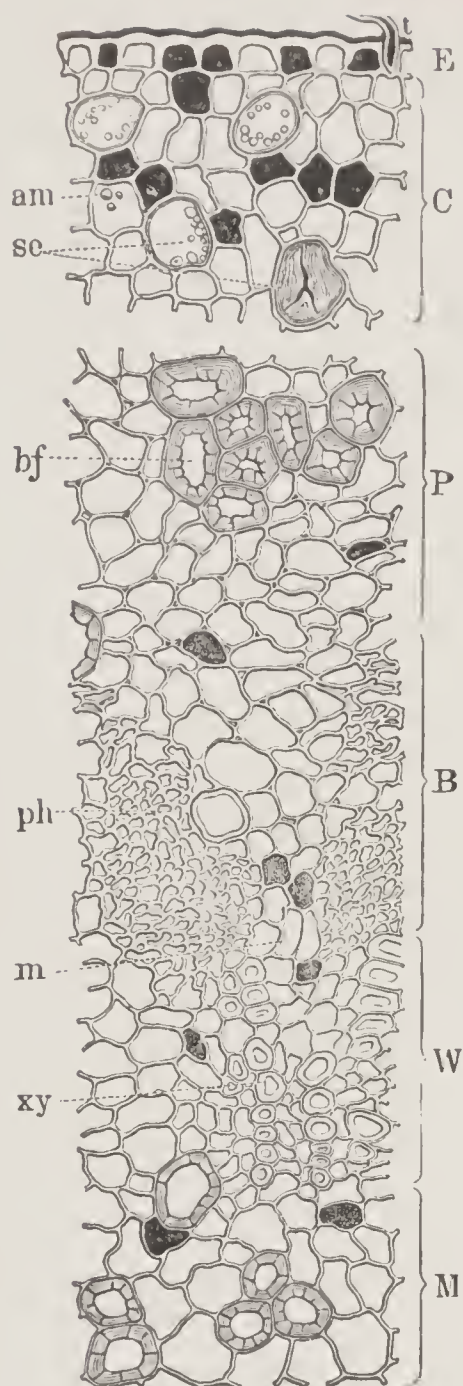


FIG. 83.—Cassia Buds. Calyx tube in cross section. *E* wax-coated epiderm with *t* hair; *C* cortex of cells with dark contents, *am* starch cells, *se* secretion cells containing volatile oil (left) or mucilage (right); *P* pericycle with *bf* bast fibers; *B* bast with *ph* phloem and *m* medullary ray; *W* wood with *xy* xylem; *M* pith of parenchyma and bast fibers. $\times 160$. (A.L.W.)

about the fruit and contracts still more abruptly at the top where it is indistinctly lobed.

The spermoderm of the single seed is grown to the endocarp.

MICROSCOPIC STRUCTURE.—Commercial cassia buds are much more complicated in structure than cassia bark, necessitating a study of stem, calyx tube, calyx lobes, sides and top of pericarp, and spermoderm.

Stem.—The slender, dry stem and lower pedicel differ from the calyx tube chiefly in that (1) the outer walls of the *epidermal cells* bow outward in a marked degree, (2) the *pericycle* forms a nearly closed ring, (3) the *xylem elements* are broader, and (4) the thickness from the epiderm to pith is less. Toward the end of the pedicel the structure is intermediate.

Calyx Tube (Fig. 83).—Six zones are well defined, at least after treatment with alkali or bleaching agents to remove the brown coloring matter which impregnates the softer tissues: (1) *epiderm* (*E*) of cells with thickened outer and radial walls and thick-walled, often crooked hairs (*t*) up to over $200\ \mu$; (2) *cortex* (*C*) of ground parenchyma containing small, rounded starch grains (*am*) and secretion cells (*se*) containing volatile oil, resin, or mucilage; (3) *pericycle* (*P*), an interrupted zone of bast fibers (*bf*); (4) *phloem* or *bast* (*B*), the more or less collapsed sieve tubes and accompanying cells forming marked groups (*ph*); (5) *xylem* or *wood* (*W*), the vessels forming groups (*xy*); and (6) *pith* or *medulla* (*M*) of parenchyma and bast fibers.

Wax granules cover the *epiderm*, forming a bloom.

The *hairs* (Fig. 84, t^1 , t^2 , t^3) differ greatly in the form of the base, breadth of lumen, and nature of the bends.

Even greater variety is noticeable in the elongated sclerenchyma elements of the pericycle, loosely grouped as *bast fibers* (Fig. 84, f^1 , f^2 , f^3 , f^4). Some are pointed, others blunt; some have thick walls and narrow lumens, others thin walls and broad lumens; some have narrow, diagonal pores, others round or oval pores. The most remarkable sclerenchyma elements are the *multicellular fibers* (f^5). These

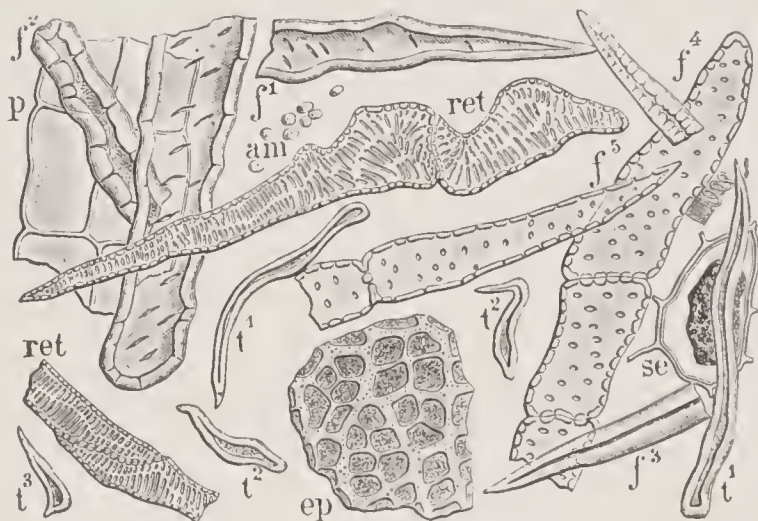


FIG. 84.—Cassia Buds. Elements of calyx in surface view. *ep* epiderm with wax granules; t^1 , t^2 , t^3 hairs; f^1 , f^2 , f^3 , f^4 unicellular bast fibers; f^5 multicellular fiber; *ret* reticulated vessels; *p* elongated parenchyma accompanying fibers; *am* starch grains; *se* secretion cell. $\times 160$. (A.L.W.)

consist of a succession of elongated sclerenchyma cells arranged end to end, the terminal members being pointed.

Curiously distorted *reticulated vessels* (Fig. 84, *ret*) occur in the xylem.

Calyx Lobes.—A striking character of both *outer* and *inner epiderm* (Fig. 84, *ep*) is the thick walls of the mother cells and the thin walls forming the daughter cells. The *fibers* are much thinner-walled than those of the tube.

Pericarp (Fig. 85).—A longitudinal radial section passing through the remains of the ovary canal (*fc*) shows (1) *epicarp* (*epi*) of palisade cells with thick outer walls and outer ends of radial walls; (2) *outer mesocarp* of parenchyma, stone cells (*st*), and secretion cells (*se*); (3) *inner mesocarp* of parenchyma, crystal cells (*cr*¹), and secretion cells (*se*), all compressed in the inner parts; and (4) *endocarp*

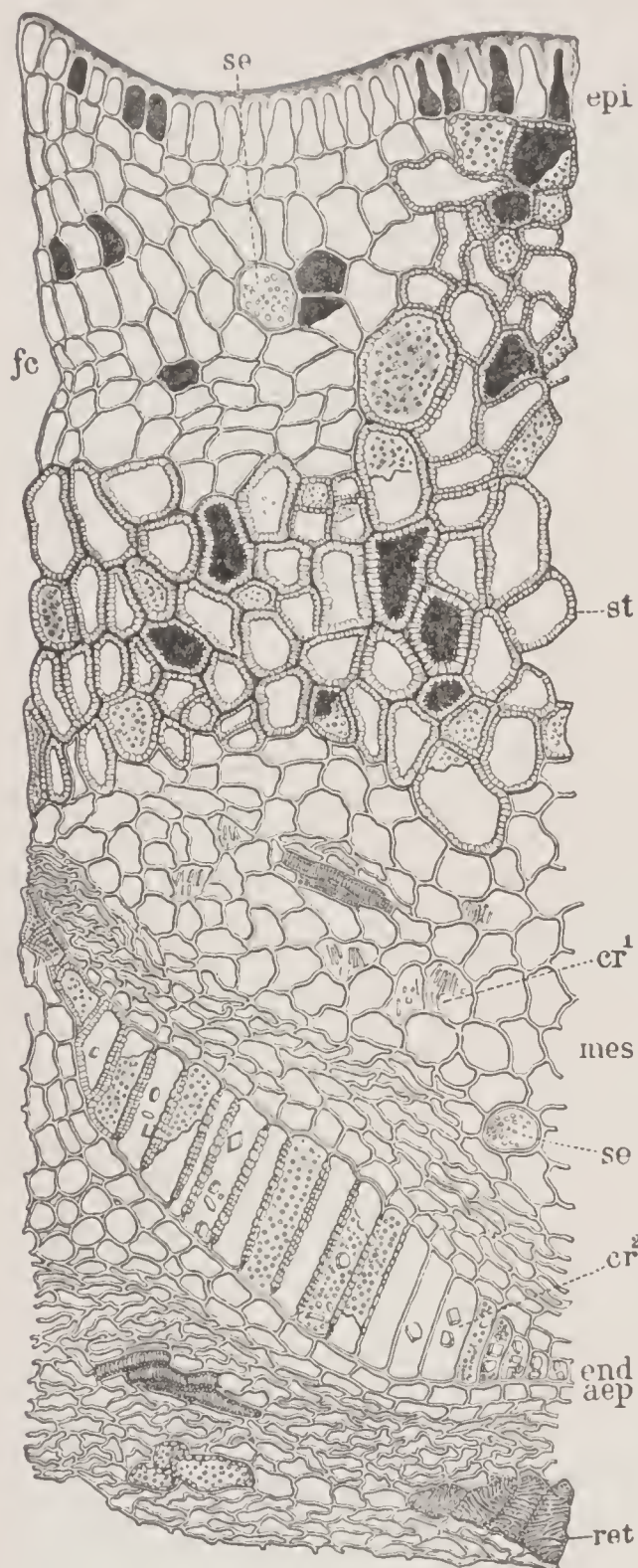


FIG. 85.—Cassia Buds. Pericarp and spermoderm in radial longitudinal section. *epi* epicarp; *st* stone cell zone; *mes* inner mesocarp with *cr*¹ crystal cells and *se* secretion cells; *fc* ovary canal; *end* endocarp containing *cr*² crystals; *aep* outer epidermis and *ret* reticulated cells of spermoderm. $\times 160$. (A.L.W.)

(*end*) of palisade sclerenchyma, narrowing abruptly at the ovary canal and passing into isodiametric parenchyma toward the edge of the dome.

The *oxalate crystals* in the mesocarp (*cr*¹) are narrow. The endocarp cells contain large isodiametric crystals (*cr*²).

Spermoderm (Fig. 85).—The *outer epidermis* (*aep*) has somewhat thickened outer walls. The middle tissues consist of parenchyma, more or less compressed, in which are the raphe bundle and, at a distance from the canal, radially elongated *reticulated cells* (*ret*).

CHIEF STRUCTURAL CHARACTERS.—Calyx urn-shaped, rough, black, nearly covering fruit.

Hairs unicellular, often crooked, thick-walled, pointed; bast fibers of various forms, breadth, and wall thickness; multicellular fibers present; secretion cells contain volatile oil, resin, or mucilage.

CHEMICAL COMPOSITION.—Proximate analyses are given in the table under Cassia, p. 264.

Pentosans.—Calculated to the dry basis, Hanus and Bien found in cassia buds 6.15 per cent of pentosans. See also Introduction to Part III.

SEEDS OF THE MUSTARD FAMILY

(*Cruciferæ*)

THE general characters of the group, tables showing the macroscopic and microscopic structure, and descriptions of the seeds used for oil production and cattle feeding are given under Oil Seeds, Volume I.

Mustard Flour, or ground mustard, is prepared by removing the hulls from the seed and grinding. A portion of the oil may or may not be removed by cold pressing. It is the common practice to mix the flour of black and white mustard; on moistening, the former contributes volatile mustard oil, the latter, sinalbin mustard oil and an excess of myrosin to supply any deficiency of enzyme in the black mustard flour. The practical test, however, is organoleptic since flavor, strength, and color are the only desiderata.

A summary of analyses of 26 brands of air-dry mustard flour by Winton, Ogden, and Mitchell¹ are given below. Although not of known origin, microscopic examination showed the flours to be mixtures in different proportions of black and white mustard flour together with small amounts of accidental impurities but no wilful admixture.

COMPOSITION OF COMMERCIAL MUSTARD FLOUR (WINTON, OGDEN, AND MITCHELL)

	Protein	Fat	Reducing matter, acid hyd.*	Reducing matter, diastase *	Fiber	Ash
	%	%	%	%	%	%
Min.	35.63	17.14	1.85	0.28	1.58	4.81
Max.	43.56	28.10	6.12	2.08	4.87	7.35
Aver.	39.57	20.61	4.33	1.07	2.58	5.99

* Calculated as starch.

¹ Connecticut Agr. Exp. Sta. Rep. 1898, p. 217.

The matter insoluble in water, yielding reducing matter by direct acid hydrolysis or by the diastase method, was calculated as starch for the reason that the figures thus obtained indicate the allowance that should be made in the determination of starch in mixtures of mustard and flour.

The percentages of volatile ether extract given in the original article are not included in the above summary for reasons stated below.

Prepared Mustard is a complex mixture of ground mustard seed or mustard flour with, usually, salt, sugar, spices, and vinegar. The presence of turmeric, contributing flavor as well as color, in a product otherwise pure, seems unobjectionable, although cases based on its presence have been tried in federal courts.

Standards. Mustard Seeds.—The U. S. Standards require that the seeds of black mustard (*Brassica nigra* (L.) Koch), brown mustard (*B. juncea* Hook f. et Th.), and white mustard (*Sinapis alba* L.) contain not over 5 per cent of total ash and 1.5 per cent of sand. In black and brown mustard the U. S. Standards require at least 0.6 per cent of volatile oil (calculated as allylisothiocyanate determined by the method specified).

Mustard Flour.—The U. S. Standards specify that the hulls be largely removed and permit the removal of a portion of the fixed oil. The limit allowed for starch is 1.5 per cent and for total ash is 6 per cent.

Prepared Mustard is described in the U. S. Standards, adopted in 1923, as “a paste composed of a mixture of ground mustard seed and/or mustard flour and/or mustard cake, with salt, a vinegar, and with or without sugar (sucrose), spices, or other condiments.” In the water-, fat-, and salt-free material not less than 5.6 per cent of nitrogen is required, and not over 24 per cent of carbohydrates (calculated as starch) and 12 per cent of fiber are permitted.

MICROSCOPY OF MUSTARD PRODUCTS AND CRUCIFEROUS CAKES.—Compare with Microscopy of Cruciferous Seeds, Volume I.

Mustard Seed unground is a common pickling spice and ingredient of mixed spices. The identification of the kind of seed and impurities involves a macroscopic comparison with known samples, supplemented by microscopic examination.

Mustard Flour.—For the preliminary examination, mounts of the material in water suffice. Foreign starchy matter, such as wheat flour, is readily detected by the starch grains and the iodine test, turmeric by yellow fragments becoming brown with alkali, charlock by the chloral hydrate test as given under Charlock, and other cruciferous

adulterants, such as common and German rape and sarson, by the characters of the hulls. Treatment with sodium hydroxide or chloralhydrate aids in clearing the specimens on the slide.

Many times the desired information is secured by the preliminary examination, but for a more exhaustive test a portion of the material should be extracted with ether or gasoline.

In case a starchy diluent or impurity is present, treatment with acid as described under wheat flour, followed by heating with 1 per cent sodium hydroxide, is desirable. Starchy material absent, it is sufficient to heat the extracted material with 1 per cent sodium hydroxide, allow to settle, decant, and examine the residue.

If crude fiber is determined, the fiber, after weighing and before ignition to determine ash, may be robbed of a few fragments for microscopic examination without appreciably affecting the accuracy of the determination, or one of the duplicate portions may be used exclusively for this purpose.

Prepared Mustard may be examined directly and after shaking or stirring with water, alcohol, and gasoline, filtering after each treatment. The microscopist must be familiar with the histological characters not only of mustard seed but of a long list of spices, including turmeric, and, if starch is present, of cereals, etc.

BLACK MUSTARD

Brassica nigra (L.) Koch = *Sinapis nigra* L.

Fr. Moutarde noire. Sp. Mostaza negra. It. Mostarda nera.
Ger. Schwarzer Senf.

Although the seed of this species, being brown rather than black, is sometimes known as brown mustard, that name is more commonly applied to other kinds, notably Sarepta mustard (*B. Besseriana* Andr.). Black mustard seed, of all the common varieties, yields the greatest amount of volatile mustard oil and consequently is the most pungent.

This species, although now widely distributed as a cultivated plant and a weed, is a native of central and southern Europe. Among the commercial varieties of seed are English, Bari, Triest, German, and California.

MACROSCOPIC STRUCTURE (Fig. 86).—Characteristic of the *pod* is its short length (less than 1.5 cm.), four angles, short beak,

and smooth surface. The globose or slightly ellipsoidal, often shrunk *seed* is the smallest of the common mustards, its greatest diameter seldom exceeding 1.7 mm. It is not jet black but various shades of brown. Fine but sharply defined reticulations are evident under the lens.

As is true of all the cultivated species of *Brassica* (mustards and rapes), the *flowers* are yellow, the *seed-pod* is narrow elongated, and the *cotyledons* of the seeds are conduplicate, the *radicle* being bent at its juncture with the cotyledons so that in cross section it is more or less circular in the reentrant angle of the V of the folded cotyledons.

MICROSCOPIC STRUCTURE.—All the standard treatises on the microscopy of both foods and drugs, beginning with Oudemans¹ and

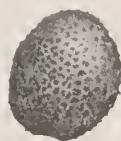


FIG. 86.

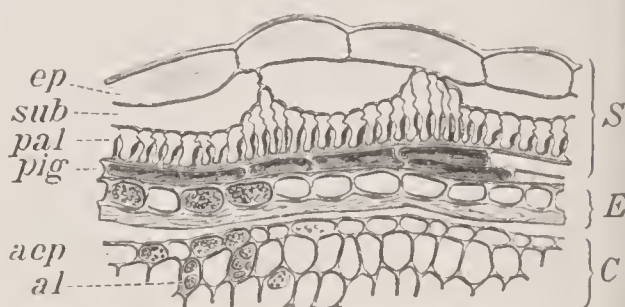


FIG. 87.

FIG. 86.—Black Mustard. Seed. $\times 8$. (A.L.W.)

FIG. 87.—Black Mustard. Seed in cross section. *S* spermoderm: *ep* outer epiderm; *sub* subepiderm; *pal* palisade cells; *pig* pigment cells. *E* endosperm. *C* cotyledon with *aep* outer epiderm and mesophyl containing *al* aleurone grains. $\times 160$. (K.B.W.)

Berg,² describe the histology of black mustard. The error made by Berg of considering the endosperm as inner spermoderm, although corrected by Harz, has been passed on to works of such well-known authors as Tschirch and Oesterle and Vogl.

Spermoderm.—Cross sections (Fig. 87, *S*) cut dry show four well-developed layers: (1) the *outer epiderm* (*ep*), 20 to 30 μ thick, consisting of mucilage cells covered with a thin cuticle; (2) large thin-walled *subepidermal cells* (*sub*), corresponding to the meshes of the seed; (3) brown *palisade cells* (*pal*) with the thick inner and especially the thin outer portions of the radial walls elongated beneath the radial walls of the subepidermal layer; and (4) one (less often two) layers of parenchymatous *pigment cells* (*pig*) with brown contents.

¹ Pharmacopœa Neerlandica, Rotterdam 1854–56.

² Anat. Atlas, Berlin, 1865, p. 91.

Gram¹ has pointed out that the *mucilage* of the epidermal cells is uniformly stratified and not with an axial cavity or column as shown by Moeller.² This may be demonstrated by cautiously drawing water into an alcohol mount. Treatment of surface mounts with sodium hydroxide brings out delicate beads in the walls.

The *reticulations* seen under a lens, corresponding to the cells of the subepidermal layer, are due partly to the somewhat rigid radial walls of that layer and partly to the greater height of the palisade cells beneath them. In surface view (Fig. 88) the palisade layer (*pal*²) shows corresponding dark reticulations, the meshes of which (maximum 110 μ) are somewhat smaller than in brown mustard. The individual palisade cells, reaching 20 μ in the longest tangential diam-

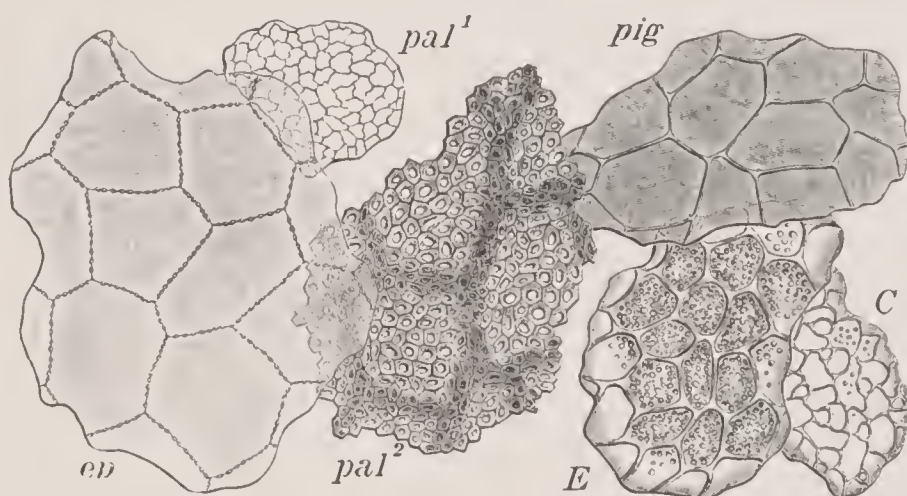


FIG. 88.—Black Mustard. Elements of seed in surface view. *ep* outer epiderm; *pal*¹ outer, *pal*² inner portion of palisade layer; *pig* pigment cells; *E* endosperm; *C* outer epiderm of cotyledon. $\times 160$. (K.B.W.)

eter and commonly less than 12 μ , are also smaller than in the last-named species. Sometimes fragments of the outer thin-walled portion of the layer break away from the thickened inner portion (*pal*¹).

Endosperm (Figs. 87 and 88, *E*).—All that remains of the endosperm at maturity is (1) the single layer of *aleurone cells*, similar to those of the cereals, which vary up to 45 μ in tangential diameter and contain aleurone grains up to 4 μ , and (2) a structureless layer of *compressed cells*.

Embryo.—A cross section of the seed shows not only the macroscopic arrangement of the radicle and the two cotyledons but the cellular structure of both.

¹ Landw. Vers.-Stat. 1898, 50, 449.

² Mikros. Nahr.-Genussm., Berlin, 1 Aufl. 1886, p. 261; 3 Aufl. 1928, p. 159.

The *outer* (lower) *epiderm* of one cotyledon (Fig. 87) abuts the endosperm for about three-fourths of its circumference while that of the other cotyledon abuts the radicle. Surface mounts (Fig. 88, C') show that although none of the cells is large some are markedly small daughter cells which are later differentiated into stomata.

Beneath the outer epiderm and in the center of the cotyledons the *mesophyl cells* are nearly isodiametric, but beneath the inner epiderm they are typical *palisade cells* in several rows. Through the central mesophyl run the *procambium bundles* which in cross section are recognized by the groups of cells, smaller than the others, occurring at more or less equal intervals.

A cross section of the radicle shows the *epiderm*, the *periderm* (cortex) forming a zone of isodiametric cells like those beneath the outer epiderm of the cotyledon, and the *central cylinder* (plerome) of small cells.

Aleurone grains and *fat* occur throughout the tissues of both cotyledons and radicle. The *aleurone grains*, examined in turpentine, seldom exceed 3 or 4 μ in the epidermal layer, but further inward they reach 10 or 12 μ , or if elongated, as often happens, may reach 20 μ in their largest diameter. Each contains numerous globoids.

Scattered among the cells of both the cotyledons and radicle containing the aleurone grains are others differentiated as *myrosin cells*. Gruinard¹ has shown that these contain grains which in sections mounted in oil differ from aleurone grains in that they are more refractive, do not contain globoids, and react differently with reagents as follows: hydrochloric acid in conjunction with 10 per cent orcin solution gives a violet color, heating with Millon's reagent a strong red color, and iodine a golden yellow, the color in both the two latter tests being more intense than that obtained with the aleurone grains. Before applying the tests the sections should be extracted to remove fat. No aleurone grains are present in these myrosin cells but a nucleus is visible. The number of the myrosin cells and the myrosin strength differ with the species.

CHIEF STRUCTURAL CHARACTERS.—Black mustard seed is the smallest of the true mustards. From charlock, which is nearly as small, it is distinguished by the reticulations seen under the lens. These reticulations are not so distinct nor are the meshes so large as in brown mustard. The seeds of the Indian plant palai are similar.

The absence of a central core in the mucilage cells on successive treatment with alcohol and water, the stronger development of the

¹ Recherches sur les téguments de la graine et en particulier du tégument séminal, Paris, 1893, p. 23.

subepidermal layer, and the smaller size of the palisade cells distinguish it from *sarepta* mustard; the presence of a well-developed outer epiderm distinguishes it from Indian mustard, also from common rape, German rape, brown sarson, and tori; the absence of radial cylinders in the epiderm and especially negative results with acid chloral hydrate distinguish it from charlock. See tables under Seeds of the Mustard Family, Volume I. All the mustards are practically alike in the structure of the endosperm and embryo.

CHEMICAL COMPOSITION.—The same constituents are determined in mustard products used for spices as in other cruciferous oil seeds used for cattle foods, but the purpose of the analysis is quite different. Richness in fat and protein are prime factors in the valuation of the cattle foods, but are of insignificant importance in the spices and condiments which serve merely for flavor. On the other hand, volatile oil, which is distasteful to cattle, is the one substance to which black mustard seed owes its value as a spice.

Analyses of black mustard seed, flour, and hulls, by Piesse and Stansell,¹ Richardson,² and Leach³ follow:

COMPOSITION OF BLACK MUSTARD SEED, FLOUR, AND HULLS

	Water	Protein	Oil, fixed	Oil, volatile	N-f. ext.	Fiber	Ash, total	Ash, soluble	Sand
	%	%	%	%	%	%	%	%	%
<i>Seed</i>									
P. and S.:									
Cambridge.....	8.52	26.50	25.54	0.47	25.45	9.01	4.98	1.11
Richardson:									
California.....	4.11	24.69	36.63	13.51	16.18	4.88
Trieste.....	4.62	25.88	39.55	13.50	10.84	5.61
Leach:									
Bari.....	5.88	25.62	37.81	0.94*	22.21	4.41	4.07	0.46	0.22
California.....	6.49	28.06	35.39	0.99*	22.01	4.21	3.84	0.45	0.21
<i>Flour</i>									
P. and S.:									
Superfine.....	4.35	29.81	36.96	1.44	20.75	3.09	5.04	1.01
Fine.....	4.52	30.25	38.02	1.50	20.31	2.06	4.84	0.98
Second.....	5.63	26.06	36.19	1.38	23.95	3.26	4.91	0.77
Leach:									
English.....	5.55	27.81	17.46	1.35*	40.32	3.28	5.58	0.27	0.08
California.....	7.23	41.99	20.64	1.59*	22.97	2.27	4.90	0.23	0.13
German.....	9.50	44.56	16.28	1.05*	21.96	2.45	5.25	0.09	0.50
<i>Hulls</i>									
Leach:									
English.....	6.83	24.31	13.81	0.77*	38.35	10.90	5.03	0.95	0.14

* By Rocser's method, corrected for error in original paper due to wrong factor.

¹ Analyst 1880, 5, 161.

² U. S. Dept. Agr., Div. Chem. 1887, Bul. 13, I, 181.

³ J. Am. Chem. Soc. 1904, 26, 1203.

Piesse and Stansell also give results for sulphur, "myrosin and albumen," soluble matter, and potassium myronate (volatile oil \times 3.571). A comparison of their analyses of the flour with their analysis of the whole seed indicates that none of the fixed oil was removed. The flour analyzed by Leach was undoubtedly made from partially defatted seed. The percentages of fiber showed that in all cases the hulls had been removed.

Richardson determined volatile ether extract by the method devised for spices containing essential oils and gives his results under the ambiguous head of "volatile oil." Aside from theoretical considerations the fact that he obtained higher results in white than in black mustard seed shows that volatile ether extract is not allyl isothiocyanate; consequently his figures are here omitted.

Leach's results on reducing matter by acid hydrolysis and by the diastase method are given under Carbohydrates.

Huber and Van der Wielen¹ report the following results obtained on black mustard seed from different countries:

	Seeds per gram	Oil, fixed	Oil, volatile
		%	%
Dutch.....	1125	25.7	1.23
North-Holland.....	976	28.0	1.15
English.....	630	31.4	1.07
Russian.....	362	37.0	0.63
Caucasian.....	1690	29.8	1.07
Italian.....	910	32.5	0.87
Sicilian.....	964	32.9	0.94
Rumanian.....	490	35.7	0.66
Bombay.....	290	33.0	1.07

It should be noted that as a rule small size was associated with a low content of fixed oil and a high content of volatile oil. This point is confirmed by Cauda,² who, however, states that the product of northern countries yields more volatile oil than that of southern countries.

Proteins.—See White Mustard.

Fixed Oil.—The fatty oils of both black and white mustard seed closely resemble rape oil. Being without a sharp taste they are suited

¹ Pharm. Weekbl. 1915, No. 39.

² Staz. sper. agr. ital. 1919, 52, 112.

after refining for salads and cooking, but are generally used only for technical purposes. Like rape oil they are good lamp oils.

Physical and Chemical Values.—Black mustard oil resembles rape oil in its values but not so closely as white mustard oil. In general, black mustard oil has a higher specific gravity and iodine number than either white mustard oil or rape oil.

VALUES OF BLACK MUSTARD OIL

	Sp. gr. 15.5° C.	Ref. ind. 25° C.	Solid. point	Maumené No.	Sapon. No.	Iodine No.	Fatty acids, titer
			°C.				°C.
Min. . .	0.917	1.4705	−18	42	173	106	6
Max. . .	0.923	1.4728	−15	58	183	126	10

Grimme,¹ in addition to values within the above limits, found in a single sample: ester number 170.6, fatty acids 94.16 per cent, acid number 2.6 (oleic acid 1.32 per cent), and unsaponifiable matter 1.18 per cent.

Volatile Mustard Oil.—Förster² in his monograph on rape cake gives a compilation of results on volatile oil in various cruciferous seeds and cakes. Results for black mustard by Dircks, Scraedler, Piesse and Stansell, Hassall, Birkenwald, Ulbricht, and Förster show a range of 0.40 to 1.89 per cent. Tsakalotos³ found 1.13 to 1.21 per cent of volatile oil in 5 samples of Greek black mustard seed. By the Von Fellenberg chromic acid oxidation method, Zäch⁴ obtained 0.5 to 1.0 per cent of volatile oil in black mustard seed.

The remarkable increase of volatile oil in rape cake (see Common Rape, Volume I) obtained by Ulbricht on addition of white mustard containing an excess of myrosin suggests that such an increase may also be obtained in the case of black mustard. This is one of several topics touching this group that seem worthy of study.

Allyl Isothiocyanate, C_4H_5NS or $CH_2 : CH \cdot CH_2 \cdot NCS$, the characteristic pungent odor of black mustard, as was first shown by Boutron and Fremy,⁵ is due to this substance formed by the action of the

¹ Pharm. Ztg. 1912, **57**, 520.

² Landw. Vers.-Stat. 1898, **50**, 371.

³ J. pharm. chim. 1916, **13**, 78.

⁴ Mitt. Lebensm. Hyg. 1932, **23**, 156.

⁵ J. pharm. chim. 1822, **26**, 468.

enzyme *myrosin* on *sinigrin* in the presence of water, as noted above. Although not present in the seed until the enzyme acts on the sinigrin, volatile mustard oil is commonly spoken of as a constituent and the amount formed by digestion with water as determined after distillation by its action with ammonia, whereby thiosinamine ($C_4H_8N_2S$) is formed, is frequently given as a measure of pungency. In mustards used as spices pungency is a desirable quality, but in rape cake and other cattle foods it is objectionable. The oil itself produces blisters on the skin and causes serious irritation if inhaled. To this substance mustard flour owes its vesicatory properties.

Allyl cyanide and *carbon disulphide* are also present in mustard oil. In an abnormal oil from *B. juncea*, Schimmel & Co.,¹ in addition to allyl cyanide, found *crotonyl mustard oil*, $CSN \cdot CH_2 \cdot CH_2 \cdot CH : CH_2$, and *dimethyl sulphide*.

Neuberg and Wagner² and Neuberg and Von Schoenebeck³ consider that *myrosinase* (myrosin) is a mixture of a sulphatase and a glucosidase which may be separated by Willstätter's adsorption method.

Sinigrin or **Potassium Myronate**, $C_{10}H_{16}KNS_2O_9 + H_2O$ or $C_{10}H_{18}KNS_2O_{10}$, a glucoside, occurs in certain cruciferous seeds, notably black and brown mustards, as well as in horseradish roots and quite probably in sharp-tasting leaves such as those of peppergrass. The peppery taste of the radish and the similar flavor of some turnips doubtless indicates the presence of this substance or a related sulphur compound. It was first isolated by Bussy,⁴ and its decomposition into allyl isothiocyanate, dextrose, and potassium hydrogen sulphate, through the action of the enzyme myrosin, was demonstrated by Will and Körner.⁵ This work and that of Gadamer⁶ justifies the following chemical formula:



Sinigrin or Potassium myronate

As prepared from black mustard seed by extraction with water after previous treatment with boiling 85 per cent alcohol, sinigrin forms glistening crystalline needles readily soluble in water, but only slightly soluble in alcohol. It has a bitter taste, but no decided odor.

¹ Rep. Oct. 1910, 81.

² Biochem. Z. 1926, **174**, 457.

³ Naturwissenschaften 1933, **21**, 404.

⁴ J. pharm. chim. 1822, **26**, 39.

⁵ Ann. Chem. Pharm. 1863, **125**, 257.

⁶ J. Pharm. 1896. **4**, 462.

Carbohydrates.—Although starch is absent in mustard seed, a small amount of *reducing matter* is obtained by the diastase method for starch determination, even in the absence of starchy impurities, and a considerable amount by direct hydrolysis, in both cases after preliminary washing to remove soluble carbohydrates. Leach¹ found in Bari and California seed by the diastase method 1.76 and 1.78 per cent and by direct hydrolysis 7.34 and 6.94 per cent respectively. In mustard flour made from English, California, and German seed the same author found respectively 0.71, 0.23, and 0.22 per cent by the diastase method and 11.89, 4.87, and 5.63 per cent by direct hydrolysis. Similar results by Winton, Ogden, and Mitchell are given above.

Pentosans.—Hanus and Bien found in the dry matter 5.93 per cent. See Introduction to Part III.

Phosphorus-Organic Compounds. *Phytin.*—See Indian Mustard.

Enzymes. *Myrosin.*—(See Sinigrin above.)

Phosphatase.—According to Courtois,² both black and white mustard, also doubtless other cruciferous seeds, contain a phosphatase that hydrolyzes α - and β -glycerophosphoric acids at the same speed at all degrees of hydrogen ion concentration.

Mineral Constituents.—The composition of the ash of a sample of Cambridge black mustard seed, as determined by Piesse and Stansell,³ is given in the table below, calculated to the pure ash by excluding charcoal and sand. The proximate analysis of the seed itself appears in a table above.

ANALYSIS OF BLACK MUSTARD SEED ASH (PIESSE AND STANSELL)

K ₂ O	Na ₂ O	CaO	MgO	Fe ₂ O ₃	P ₂ O ₅	SO ₃	SiO ₂	Cl
%	%	%	%	%	%	%	%	%
23.59	0.38	14.95	11.06	1.16	40.99	6.12	1.55	0.16

¹ Loc. cit.
² Compt. rend. 1934, **199**, 1252.
³ Loc. cit.

SAREPTA OR BROWN MUSTARD

Brassica Besseriana Andr. = *B. juncea* (L.) Coss. = *Sinapis juncea* L.

Fr. Moutarde brune. It. Mostarda bruna. Sp. Mostaza baza.
Ger. Sarepta-Senf.

The mustard grown in Russia and known for years in Europe as Sarepta mustard was quite generally confused with Indian mustard (asi-rái). Tschirch and Oesterle, Vogl, and other authors, under the head of Sarepta mustard, erroneously give the Latin name of the Indian species.

Prain,¹ after numerous cultural experiments, showed that asi-rái is *B. juncea* Hook f. et Thom. and cooperated with Kinzel² in determining whether that species was grown commonly in Europe. After microscopic studies of authentic material from India and Russia, Kinzel proved that Sarepta mustard is *B. Besseriana* and that the Indian species is unknown in Europe as a farm crop.

Danish mustard (*B. lanceolata* Lange) is now regarded as identical with *B. Besseriana*.

The brown mustard occurring with charlock as a weed in the grain fields of Minnesota, North and South Dakota, and neighboring regions corresponds in the histology of its seed with *B. Besseriana*. Although the seed yields less volatile oil than black mustard it is of much greater value as a spice than charlock which yields none. Winton and Bornmann³ have shown that the volatile oil strength of wild mustard seed separated from screenings may be quite accurately calculated from the botanical analysis.

Although wild mustard seed is obtained quite free from impurities by special machinery described below under charlock, the separation of its two component seeds, brown mustard and charlock, is commercially impossible.

MACROSCOPIC STRUCTURE.—The seed is somewhat larger than black mustard seed, often reaching a maximum diameter of 2 mm. It also is lighter in color and has larger and more pronounced reticulations. These distinctions although characteristic for the pure seeds are not sufficiently marked to identify every seed in a mixture of the two mustards. The separation of brown mustard from charlock is, however, readily accomplished under a lens owing to the absence of reticulations on the charlock.

¹ Agr. Ledger 1898, No. 1.

² Landw. Vers.-Stat. 1899, 52, 169.

³ J. Ind. Eng. Chem. 1915, 7, 684.

MICROSCOPIC STRUCTURE.—In cross section (Fig. 89, *S*) two layers appear different from the corresponding layers of black mustard: (1) the *subepidermal layer* (*sub*), the cells of which are not so high in the center; and (2) the *palisade cells* (*pal*) which have the thickened inner portions higher in parts, forming the reticulations of the seed. This inequality of the thickened walls more than offsets the greater uniformity of the thin outer portions of the walls, making the network on the whole more conspicuous.

Another distinguishing characteristic is the ragged or dentate outline of the thickenings as seen in cross section.

Surface preparations (Fig. 90) bring out three distinctions from black mustard: (1) the concentric rings of mucilage about a central core in the *epiderm* (*ep*), seen on adding water to alcohol mounts;



FIG. 89.—Serepta Mustard. Seed in cross section. *S* spermoderm: *ep* outer epiderm; *sub* subepiderm; *pal* palisade cells; *pig* pigment cells. *E* endosperm. *C* cotyledon with *aep* outer epiderm and mesophyl containing *al* aleurone grains. $\times 160$. (K.B.W.)



FIG. 90.—Serepta Mustard. Elements of seed in surface view. *ep* outer epiderm; *pal* palisade cells; *pig* pigment cells; *E* endosperm; *C* outer epiderm of cotyledon. $\times 160$. (K.B.W.)

(2) the larger *palisade cells* (*pal*) which reach a maximum of 27μ ; and (3) the larger meshes of the *reticulations* or dark network in the palisade layer.

CHIEF STRUCTURAL CHARACTERS.—The larger seed, often 2 mm. in diameter, and the more distinct reticulations distinguish it from black

mustard and Indian mustard; the presence of reticulations, from charlock, Indian mustard, and brown sarson.

Microscopic distinction from black mustard in powder form depends chiefly on the large size of the palisade cells and the larger meshes of the reticulations. The concentric rings about the central core in the mucilage cells require careful manipulation for their demonstration. On warming in acid chloral hydrate no carmine color is formed as in charlock. The presence of a distinctly cellular epiderm distinguishes the seed from Indian mustard, brown sarson, and tori. See tables under Seeds of the Mustard Family, Volume I.

CHEMICAL COMPOSITION.—A sample of "Sarepta Mustard (*B. juncea*)" analyzed by Birkenwald¹ was doubtless from *B. Besseriana*.

Water	Protein	Oil, fixed	Oil, volatile	Ash	S	P ₂ O ₅	N
%	%	%	%	%	%	%	%
7.63	26.31	31.40	1.67	4.52	0.54	1.89	4.21

Volatile Mustard Oil.—Kinzel² found 0.92 and 0.89 per cent in authentic samples.

Winton and Bornmann,³ in wild mustard seed separated from flax-seed grown in North Dakota, found by botanical analysis 99.5 per cent of brown mustard seed with the microscopic characters of *B. Besseriana*. The seed contained 0.82 per cent of volatile mustard oil.

INDIAN MUSTARD

Brassica juncea Hook. f. et Thom.

This species, according to Prain,⁴ is grown in place of black and white mustard in India where it is known as *rái* or *asi-rái*. Kinzel,⁵ after careful microscopic investigation of Indian and European mustards, reached the conclusion that this species is not grown as a field crop in Europe.

¹ Dis. Dorpat; Schw. W. 26, 277.

² Loc. cit.

³ J. Ind. Eng. Chem. 1915, 7, 684.

⁴ Agr. Ledger 1898, No. 1.

⁵ Landw. Vers.-Stat. 1899, 52, 169.

Prain described three varieties grown during the cooler part of the year on the Indian plains and the foot-hill region of the Himalayas: (1) *Jhuni* (*Sinapis ramosa* Roxb.), grown in Hughli district of Bengal; (2) *Lalki Tori*, grown in Shahabad district of Bihar; and (3) *Kazli Sarishá*, grown in 24-Parganas (Alipur) district, Bengal.

MACROSCOPIC STRUCTURE.—The plant of the third variety is distinguished from the first two by its rough hairs and earlier ripening. The seeds of the first variety (*Jhuni*) vary up to 2 mm. in diameter, being about the same size as the seed of *Sarepta* mustard; those of the two other varieties are larger, varying up to 2.5 mm. Under a lens the reticulations of the first two varieties are distinct, of the last variety (*Kazli Sarishá*) are very indistinct.

MICROSCOPIC STRUCTURE.—Our observations confirm those of Kinzel. No cellular structure is evident in the *outer epiderm* and *subepiderm* in any of the three varieties. Otherwise the seed is indistinguishable from that of *Sarepta* mustard except that in the third variety (*Kazli Sarishá*) the variation of the height of the *palisade cells* is slight and consequently the dark reticulations seen in surface view are indistinct.

CHIEF STRUCTURAL CHARACTERS.—The chief distinction from *Sarepta* mustard, common to all three varieties of Indian mustard, is the absence of evident cellular structure in the epiderm. The seeds of the different varieties differ in size (maximum 2 to 2.5 mm.) and in distinctness of the reticulations. They resemble closely seeds of *Sarepta* mustard. See tables under Seeds of the Mustard Family, Volume I.

CHEMICAL COMPOSITION.—Although the name *S. juncea* often has been misapplied to *B. Besseriana* (*Sarepta* mustard), the following analysis of Werenskiöld¹ appears to apply to the true Indian species.

COMPOSITION OF INDIAN MUSTARD SEED (WERENSKIÖLD)

Water	Protein	True protein	Oil, fixed*	Oil, volatile†	Lecithin‡	N-f. ext.	Sucrose, grav.	Sucrose, polar.	Fiber	Ash
%	%	%	%	%	%	%	%	%	%	%
6.16	24.63	21.57	35.51	0.58	2.04	20.38	1.00	1.24	8.00	5.32

* Ether extract. † Schlicht method. ‡ Schulse and Frankland method.

Fixed Oil.—Grimme² reports the following results on *B. juncea* Hook f. et Thom. which is assumed to be the true species: specific

¹ Tidskr. norske Landwbr. 1895, 2, 273.

² Pharm. Ztg. 1912, 57, 520.

gravity at 15° C. 0.9206, refractive index at 25° C. 1.4705, solidifying point -12 to -11° C., saponification number 174.4, iodine number 106.8, ester number 172.2, acid number 2.2 (oleic acid 1.11 per cent), fatty acids 94.24 per cent, and unsaponifiable matter 1.04 per cent. On the fatty acids he obtained: refractive index at 25° C. 1.6309, solidifying point 13 to 15° C., melting point 17 to 18° C., acid number 177.7, iodine number 109.3, and mean molecular weight 315.8.

Composition of Fatty Acids.—Sudborough, Watson, Ayyar, and Mascarenhas¹ determined the individual acids in the fatty acids of the original and the hardened oil with the results tabulated below.

Acid	Original	Hardened
	%	%
Lignoceric.....	1.1	1.1
Behenic.....	3.8	46.3
Stearic.....	0.0	52.1
Myristic.....	0.5	0.5
Erucic.....	41.5
Oleic.....	32.3
Linolic.....	18.1
Linolenic.....	2.7
	100.0	100.0

Volatile Mustard Oil.—Kinzel² found the volatile oil content in 3 varieties to be: Jhuni 1.06; Lalki Tori 0.85, 0.92, and 0.79; and Kazli Sarishá 0.57 per cent.

Phosphorus-Organic Compounds. *Phytin.*—Studies by Clarke³ on a mixture of Indian seeds from *B. juncea* and *B. campestris* led to the conclusion that phytin is not a simple salt of inositolphosphoric acid but a complex calcium-magnesium salt of that acid and phosphoric acid which on liberation from the bases yields about equal amounts of the two acids. The pure phytin did not correspond to any calcium-magnesium salt of a simple acid ester of inositol and phosphoric acid, although the strychnine salt of the organic phosphoric acid isolated from the mixture of acids obtained from the phytin was analogous to salts of simple inositolphosphoric acids.

¹ J. Indian Inst. Sci. 1926, 9A, 43.

² Landw. Vers-Stat. 1899, 52, 169.

³ J. Chem. Soc. 1914, 105, 535.

Anderson and also Rather, who have studied phytins of cereals and various oil seeds, do not appear to have extended their work to cruciferous seeds.

CHINESE MUSTARD

Brassica juncea Coss. = *B. ramosa* Roxb. = *Sinapis chinensis* L.

Jap. Taka-na.

Chin. Kai-choi.

A description of the plant which is used as a vegetable is given under Leaf Vegetables, Volume II. Various forms formerly given specific names are now included under this species. That the seed is more appropriately classed as a mustard than a rape is indicated by its sharp taste as noted by Kondo,¹ as well as its content of volatile oil.

MACROSCOPIC STRUCTURE.—The *seed* examined by Kondo¹ was brown or wine red, 1.3 to 1.8 mm. long, and the weight of 1000 seeds was 1.43 grams. Its small size is noteworthy. The reticulations are very large and distinct.

MICROSCOPIC STRUCTURE.—Examination by Kondo¹ and Gram² showed practically the same structure as that of Chinese rape.

CHEMICAL COMPOSITION.—Werenskiold³ gives the composition of the seed as follows:

COMPOSITION OF CHINESE MUSTARD SEED (WERENSKIOLD)

Water	Pro- tein	True pro- tein	Oil, fixed *	Oil, vola- tile †	Leci- thin ‡	N-f. ext.	Su- crose, grav.	Su- crose, polar.	Fiber	Ash
%	%	%	%	%	%	%	%	%	%	%
6.14	22.44	18.94	39.05	0.39	3.45	21.02	0.80	0.97	6.80	4.55

* Ether extract. † Schlicht method. ‡ Schulse and Frankland method.

Fixed Oil.—Grimme⁴ obtained the following values: specific gravity at 15.5° C. 0.9230, refractive index at 25° C. (recalculated) 1.4718, solidifying point — 14° C., saponification number 177.3, iodine number 103.3, ester number 174.1, fatty acids 94.28 per cent, acid number 3.2

¹ Ber. Ohara Inst. landw. Forsch. 1917, 1, 142.

² Landw. Vers.-Stat. 1898, 50, 449.

³ Tidskr. norske Landw. 1895, 2, 273.

⁴ Pharm. Ztg. 1912, 57, 520.

(equivalent oleic acid 1.63), and solidifying point of fatty acids 14 to 15° C.

Volatile Mustard Oil.—Kinzel¹ found in the seed 0.91 per cent of volatile mustard oil.

WHITE MUSTARD

Brassica alba (L.) Boiss. = *Sinapis alba* L.

Fr. Moutarde blanche. Sp. Mostaza blanca. It. Mostarda bianca.
Ger. Weisser Senf.

White mustard differs materially from black mustard in structure and composition. Although known as white mustard, yellow is a more accurate designation. The plant is a native of Europe. It is cultivated in Holland, Germany, England, California, Argentina, and other regions.

MACROSCOPIC STRUCTURE.—The *pod* is hairy, half its length consisting of a flattened beak. The *seed* (Figs. 91, 92) is light buff, very indistinctly reticulated under a lens. It is noticeably larger than

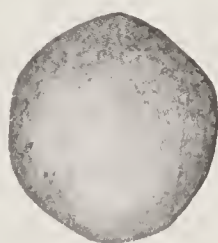


FIG. 91.

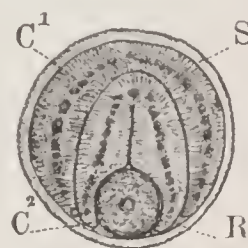


FIG. 92.

FIG. 91.—White Mustard. Seed. $\times 8$. (A.L.W.)

FIG. 92.—White Mustard. Seed in cross section. *S* spermoderm; *C*¹ and *C*² conduplicate cotyledons showing elementary bundles as dark spots; *R* radicle. $\times 10$. (K.B.W.)

any of the other common mustards, often exceeding 2.5 mm. and in exceptional cases reaching 3 mm. As is true of other light-colored mustards and rapes, an occasional seed is brown.

MICROSCOPIC STRUCTURE. Spermoderm (Fig. 93 *S*; Fig. 94).—All four layers of a typical cruciferous seed are represented: (1) the *outer epiderm* (*ep*) with mucilage in layers about a central cavity, (2) a double *subepidermal layer* (*col*) of well-developed collenchyma-like cells, (3) colorless *palisade cells* (*pal*¹ and *pal*²) thickened in the

¹ Landw. Vers-Stat. 1899, 52, 169.

inner portion, and (4) *parenchyma* (*p*) of thin-walled cells without colored contents.

The *epidermal cells* in surface view have finely beaded walls. Alcohol mounts treated with water show the character of the mucilage. Especially characteristic is the *subepidermal layer* which is strongly thickened at the angles. The *palisade cells* reach $25\ \mu$ in tangential diameter. They vary sufficiently in height to form a distinct dark network when the layer is examined under the microscope, although under a lens the seed is very indistinctly reticulated. This difference is easily explained. As shown in Fig. 93, the double layer of rather thick-walled cells of the subepidermal layer and the relatively high epidermal cells stiffened with mucilage do not sink down into the depressions formed by the outer walls of the pali-

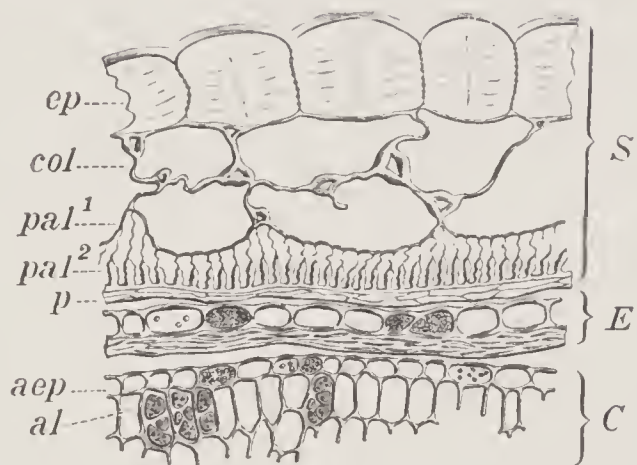


FIG. 93.—White Mustard. Seed in cross section. *S* spermoderm: *ep* outer epiderm; *col* collenchyma-like subepiderm; *pal*¹ outer thin-walled, *pal*² inner thick-walled portion of palisade layer; *p* parenchyma. *E* endosperm. *C* cotyledon; *aep* outer epiderm; mesophyl containing *al* aleurone grains. $\times 160$. (K.B.W.)

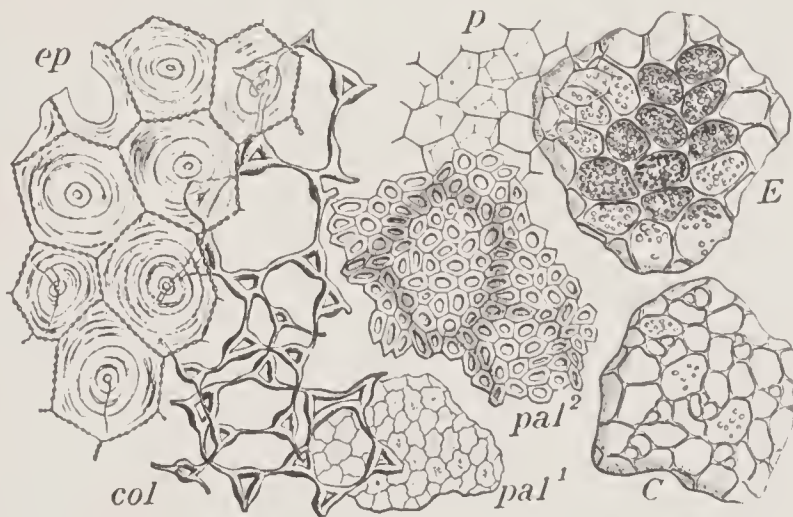


FIG. 94.—White Mustard. Elements of seed in surface view. *ep* outer epiderm; *col* collenchyma-like subepiderm; *pal*¹ outer, *pal*² inner portion of palisade layer; *p* parenchyma; *E* endosperm; *C* outer epiderm of cotyledon. $\times 160$. (K.B.W.)

sade cells to such an extent as, for example, in black mustard (Fig. 87) where the subepiderm is a single layer with thin walls and the

epidermal cells are low. The dark network of the palisade layer seen under the microscope is due partly to the greater height of the thickened portion of the radial walls and partly to the steeper outer walls forming a greater obstruction to the light.

Endosperm and Embryo (Figs. 93 and 94, *E, C*).—Practically the same as in black mustard.

CHIEF STRUCTURAL CHARACTERS.—White mustard seed is distinguished from other mustards by the large size, light buff color, and very faint reticulations. Its distinction from sarson depends chiefly on differences in microscopic structure.

The epidermal cells are high with mucilage in concentric rings about a central core. Still more striking and characteristic in both cross section and surface view is the double layer of collenchymalike cells forming a subepidermal layer (distinction from other mustards and sarson). A distinct dark network characterizes the otherwise light-colored palisade layer.

See tables under Seeds of the Mustard Family, Volume I.

CHEMICAL COMPOSITION.—No marked difference in the composition of white and black mustard seed, other than in the active principles, has been established. As in the case of black mustard, the usual proximate analysis is of chief interest to the manufacturer who takes into account the yield of oil, flour, and hulls.

References to the papers containing the analyses given in the following table will be found under black mustard.

The composition of commercial mustard flour consisting of mixtures of flour made from both black and white mustard seed is given under the head of Black Mustard.

Proteins.—The chief protein of mustards and rapes appears to be a *globulin* briefly described by Weyl.¹

Fixed Oil. Physical and Chemical Values.—The oil resembles closely rape oil. Although most of the values of white mustard oil overlap those of black mustard, the specific gravity and the iodine number are usually lower. The maximum specific gravity in the table is the only result above 0.916 found in the literature. The iodine number seldom exceeds 100, while that of black mustard is seldom below 100 and often exceeds 110.

Grimme² in addition to the values included in the above limits found in a single sample: ester number 175.2, fatty acids 94.23 per

¹ Z. physiol. Chem. 1877, 1, 72.

² Pharm. Ztg. 1912, 57, 520.

COMPOSITION OF WHITE MUSTARD SEED, FLOUR, AND HULLS

	Water	Pro- tein	Oil, fixed	Oil, volatile	N-f. ext.	Fiber	Ash, total	Ash, soluble	Sand
	%	%	%	%	%	%	%	%	%
<i>Seed</i>									
P. and S.:									
Yorkshire.....	9.32	28.37	25.56	0.06	21.66	10.52	4.57	0.55
Cambridge.....	8.00	28.06	27.51	0.08	22.86	8.87	4.70	0.75
Richardson:									
California.....	4.83	31.13	31.96	17.62	8.50	5.96
English.....	3.11	30.25	31.51	24.16	6.90	4.07
.....	5.57	28.88	33.56	22.30	5.40	4.29
.....	3.33	25.56	34.83	22.00	9.05	5.23
Leach:									
California.....	6.82	29.50	28.64	0.00	25.71	5.28	4.05	0.57	0.42
English.....	6.43	24.75	27.45	0.00	32.05	4.95	4.37	0.52	0.16
Dutch.....	5.93	25.75	30.84	0.00	26.12	6.53	4.83	0.73	0.33
German.....	6.69	31.81	27.19	0.00	25.10	4.87	4.34	0.63	0.56
<i>Flour</i>									
P. and S.:									
Superfine.....	6.30	31.56	37.18	0.03	17.84	3.90	4.22	0.44
Fine.....	5.78	30.56	35.74	0.04	19.46	4.15	4.31	0.55
Second.....	6.06	26.56	32.55	0.03	21.19	9.34	4.30	0.33
Leach:									
California.....	5.09	38.81	25.95	23.25	2.21	4.69	0.22	0.29
German.....	7.47	46.50	12.65	26.78	1.87	4.73	0.18	0.35
<i>Hulls</i>									
Leach:									
California.....	9.12	22.50	7.79	16.08	4.59	1.78	0.05
German.....	8.46	18.12	6.17	18.95	4.66	1.80	0.04

VALUES OF WHITE MUSTARD OIL

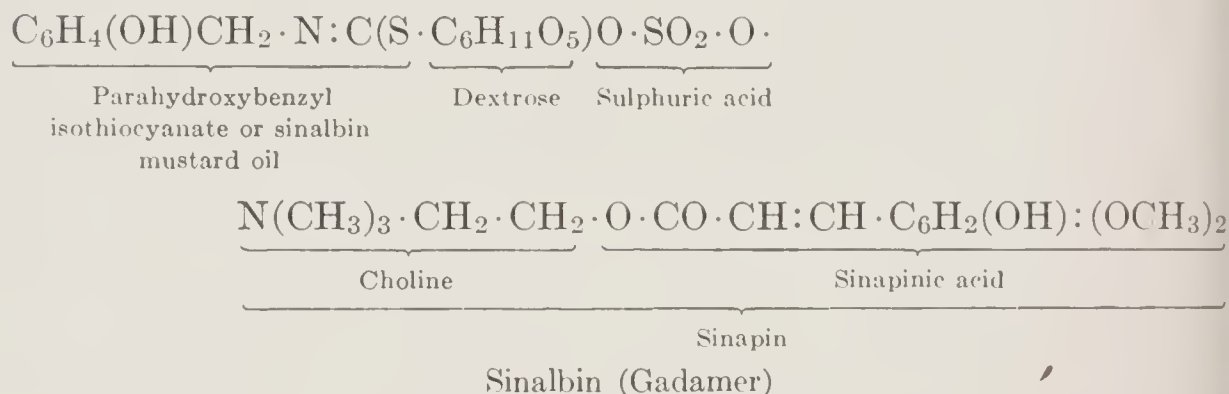
	Sp. gr. 15.5° C.	Ref. ind. 25° C.	Solid. point	Mau- mené No.	Sapon. No.	Iodine No.	Fatty acids, titer
			°C.				°C.
Min.....	0.912	1.4703	-17	44	170	92	9
Max.....	0.921	1.4732	-8	50	178	103	10

cent, acid number 2.6 (oleic acid 1.32 per cent), and unsaponifiable matter 0.98 per cent.

Volatile Mustard Oil.—*Sinigrin* appears to be absent or present only in very small amount. Any volatile oil found on analysis may be explained as due largely to analytical error or the presence of impurities such as black mustard seed. Analyses compiled by Förster

show a range of from a trace to 0.084 per cent. Zäch,¹ by Von Fellenberg's chromic acid oxidation method, obtained 0 to 0.3 per cent.

Sinalbin, $C_{30}H_{42}N_2S_2O_{15} + 5H_2O$, occurs in white mustard in place of the sinigrin of black mustard. By its discoverers, Henry and Garot,² it was called sulphosinapsin and later it was erroneously identified by Von Babo and Hirschbrunn³ as sinipin thiocyanate, an error that has been passed down in the literature and has even led to faulty analytical methods such as that used by Hassall.⁴ Robiquet and Boutron-Charland⁵ brought out the distinction of sinalbin from sinipin thiocyanate, Will and Laubenheimer⁶ determined its formula, and Gadamer⁷ derived its constitution and that of its derivative sinalbin mustard oil. The following structural formula, based on Gadamer's results, shows the parts derived from its four components with elimination of three molecules of water:



Properties.—Sinalbin is a non-volatile crystalline glucoside, somewhat soluble in water, less so in alcohol. Over sulphuric acid, it loses readily four molecules of water of crystallization, whereas the remaining molecule goes off slowly in the cold, but more rapidly on heating. Some authors join the tightly combined molecule of water to its formula.

Sinalbin Mustard Oil, C_7H_7ONCS or $C_6H_4 : (OH)CH_2 \cdot NCS$.—Like the sinigrin of black mustard, sinalbin does not itself impart the pungent flavor to the condiment, but is split up by the enzyme *myrosin*, the products in the present case being *parahydroxybenzyl isothiocyanate* or sinalbin mustard oil, a non-volatile substance with

¹ Mitt. Lebensm. Hyg. 1932, **23**, 156.

² J. Chim. med. **1**, 439 and 467.

³ Ann. 1852, **84**, 10.

⁴ Arch. Pharm. 1877, **3**, 10, 156.

⁵ J. pharm. 1873, **17**, 279.

⁶ Ann. 1879, **199**, 150.

⁷ Arch. Pharm. 1897, **235**, 83.

a pungent taste but without a pungent odor, sinapin hydrogen sulphate ($C_{16}H_{24}NO_5 \cdot HSO_4$), and dextrose ($C_6H_{12}O_6$).

Sinapin, $C_{16}H_{24}NO_5 \cdot OH$, is a hypothetical base, known only in compounds such as the hydrogen sulphate and the sulphocyanide.

Sinapinic acid, $C_{11}H_{12}O_5$ or $(CH_3O)_2 : C_6H_2OH \cdot CH : CH \cdot COOH$, is a yellowish crystalline substance, melting at 191 to 192° C., soluble in hot alcohol but difficultly soluble in water and ether.

No accurate method for the quantitative determination of sinalbin or sinalbin mustard oil has yet been devised.

Hassall determined the volatile oil, the total nitrogen, and the total sulphur and then assumed erroneously that sinalbin is sinapin thiocyanate, that myrosin and albumen are the only proteins present, and that these two have the same composition. With these data he calculated the percentages of "myrosin and albumen" and "acid salt." Naturally the results by such a method are valueless.

Förster¹ suggests a method based on the formation of sodium sulphate and sodium thiocyanate on boiling with alkali, but does not go into detail. A method depending on one of the color reactions he names, such as the intense yellow with a trace of alkali or the transitory red with nitric acid, might perhaps be devised.

Lacking a method we are left in ignorance of the sinalbin content of cruciferous seeds.

Carbohydrates.—In white mustard seed, flour, and hulls, as analyzed by Leach,² the following percentages of *reducing matter*, calculated as dextrose, were obtained by the diastase method and by direct inversion respectively: German seed 1.45 and 9.35, Dutch seed 1.82 and 10.06, English seed 0.92 and 8.42, and California seed 1.15 and 9.60 per cent; German flour 0.23 and 6.12, California flour none and 5.75 per cent; and California hulls 3.70 and 19.90, German hulls 2.91 and 17.75 per cent.

Pentosans.—In dry matter 6.58 per cent. See also Introduction to Part III.

Phosphorus-Organic Compounds. *Phytin.*—See Indian Mustard.

Enzymes.—See Black Mustard.

Mineral Constituents.—James, Way and Ogston, and other early agricultural analysts made analyses of the ash of cruciferous seeds including white mustard which are quoted in the works of Liebig, Wolff, and others.

¹ Landw. Vers.-Stat. 1898, 50, 371.

² J. Am. Chem. Soc. 1904, 26, 1203.

Piesse and Stansell¹ in addition to making the proximate analyses of Yorkshire and Cambridge seed shown above determined the ash constituents. Their results together with an analysis by Way and Ogston (1850) quoted by them follow:

ANALYSIS OF WHITE MUSTARD SEED ASH

	K ₂ O	Na ₂ O	CaO	MgO	Fe ₂ O ₃	P ₂ O ₅	SO ₃	SiO ₂	Cl
	%	%	%	%	%	%	%	%	%
P. and S.:									
Yorkshire.....	24.98	0.21	15.79	9.58	1.38	38.48	8.28	1.17	0.12
Cambridge...	22.64	0.25	11.19	12.58	1.23	41.97	8.58	1.34	0.14
W. and O.:									
White.....	25.78	0.33	19.10	5.90	0.39	44.97	2.19	1.31	trace

CHARLOCK

Brassica arvensis (L.) Ktze. = *Sinapis arvensis* L. = *B. Sinapistrum* Boiss.

Fr. Moutarde sauvage. Sp. Alhacena. It. Senape selvatica.
Ger. Ackersenf.

Authorities agree that charlock, although introduced from Europe, is one of the worst weeds in grain fields of the New World. The traveler through the states of Minnesota and the Dakotas and the neighboring provinces of Canada is impressed by the yellow color imparted to the vast fields of grain by the flowers of this weed and brown mustard. Its occurrence is by no means limited to the Northwest or to wheat fields. Selby² finds it among the very worst weeds known to the Ohio farmer, especially in oat fields. It is particularly troublesome because of the long season of ripening which, according to Wilson,³ extends in Minnesota from June to November. Spraying with copper or iron sulphate is employed for its eradication.

Seeds of "wild mustard" of the wheat fields, consisting of charlock and Sarepta or brown mustard, the former predominating, are harvested with the grain and together with other seeds and impurities of

¹ Analyst 1880, 5, 161.

² Ohio Agr. Exp. Sta. 1906, Bul. 175, 330.

³ Minnesota Agr. Exp. Sta. 1906, Bul. 95.

about the same size are separated from it by sifting. The screenings thus obtained are then run through ingenious machines for the removal of mustard seed, advantage being taken of the spherical form of the seeds which permits them to roll away from other seeds and broken grain.

The belt machines are of simple construction, the screenings being delivered in a thin broad stream onto a moving belt so inclined that the mustard seeds roll down and off, whereas the remainder of the mixture is carried upward and falls off when the belt turns. In disk machines the screenings fall on a moving horizontal disk sloped toward the center where the mustard seeds roll into a chute. A still simpler machine consists of a stationary metal spiral with three parallel troughs. The stream of screenings drops into the central trough and the constituents roll downward at different rates of speed according to their form. The spherical mustard seeds, moving most rapidly by centrifugal force, jump first into the middle and finally into the outer trough.

So efficient are these machines that mustard seed containing less than 1 per cent of impurity may be secured, although commonly this degree of purity is not attained.

Eight samples of wild mustard from wheat taken by Winton and Bornmann¹ from flour mills (7 in Minneapolis and 1 in Chicago) contained 57 to 97.2 per cent of charlock calculated free from foreign seeds. Two samples from barley separated at Milwaukee and Minneapolis contained respectively 89.1 and 95.1 per cent of charlock, while one from flaxseed, separated at Devil's Lake, North Dakota, on the other hand, contained only 0.5 per cent, the remainder in each case being brown mustard.

The removal of wild mustard from agricultural seeds is especially important. Three samples from Chicago and Minneapolis seed warehouses thus removed contained from 69.9 to 90.8 per cent of charlock.

MACROSCOPIC STRUCTURE (Fig. 95).—The nearly smooth but knotty *pod* has a beak from half to a third its length. Charlock *seeds* are about the same size as those of black mustard (maximum 1.5 mm.), but are distinguished when mature by their darker brown or black mat spermoderm and the absence of reticulations.

MICROSCOPIC STRUCTURE.—Of special value are the papers by Burchard² and Gram.³

¹ J. Ind. Eng. Chem. 1915, 7, 684.

² J. Landw. 1894, 42, 125; 1896, 44, 337.

³ Landw. Vers.-Stat. 1898, 50, 449.

Spermoderm (Fig. 96, *S*; Fig. 97).—Cross sections and surface mounts show four layers: (1) the *outer epiderm* (*ep*) of polygonal beaded cells with a central cavity surrounded by cylinders of mucilage

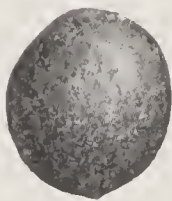


FIG. 95.

FIG. 95.—Charlock. Seed. $\times 8$. (A.L.W.)

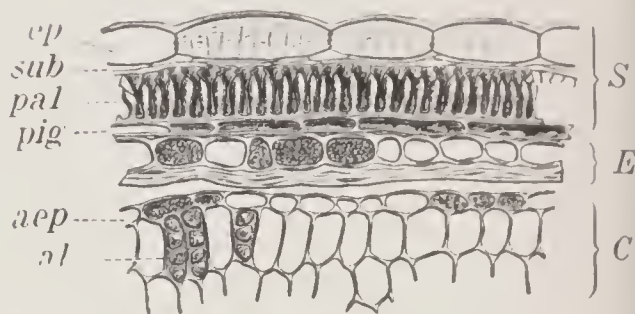


FIG. 96.

FIG. 96.—Charlock. Seed in cross section. *S* spermoderm: *ep* outer epiderm; *sub* subepiderm; *pal* palisade cells; *pig* pigment cells. *E* endosperm. *C* cotyledon: *aep* outer epiderm; mesophyl containing *al* aleurone grains. $\times 160$. (K.B.W.)

lage; (2) the *subepidermal layer* (*sub*) of two layers, more or less compressed, of thin-walled cells with intercellular spaces; (3) the *palisade layer* (*pal*) of narrow cells (up to $15\ \mu$) with deep black

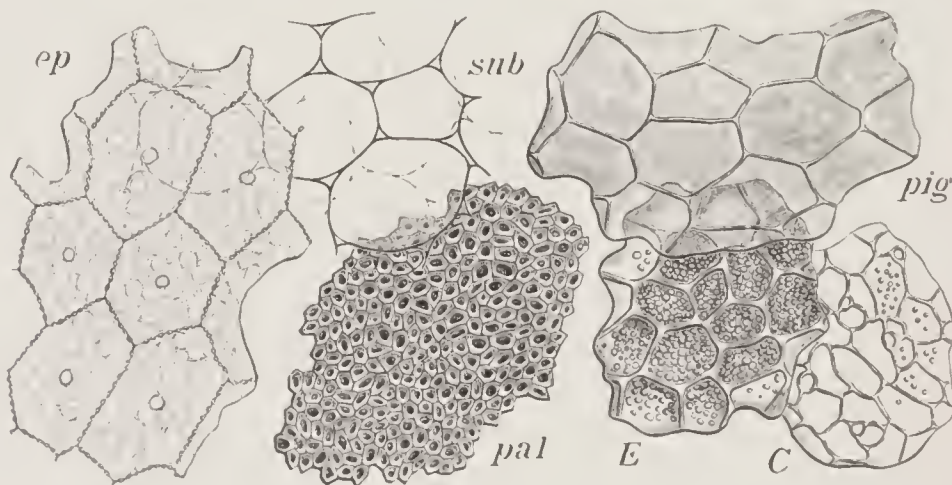


FIG. 97.—Charlock. Elements of seed in surface view. *ep* outer epiderm; *sub* subepiderm; *pal* palisade cells; *pig* pigment cells; *E* endosperm; *C* outer epiderm of cotyledon. $\times 160$. (K.B.W.)

contents becoming carmine on warming with acid chloral hydrate; and (4) the yellow-brown *pigment layer* (*pig*), one cell thick.

As in other mustards, the structure of the contents of the mucilage cells is seen on successive treatment with alcohol and water.

The carmine color produced in the contents of the palisade cells, first brought out by Waage,¹ was long thought to be due to the action

¹ Ber. Pharm. Ges. 1893, 153.

of the chloral hydrate on the pigment until it was shown by Winton¹ that the hydrochloric acid formed in chloral hydrate solution on standing causes the change in color. Fresh neutral solution of chloral hydrate does not give the reaction; on the other hand glycerin or zinc chloride acidified with hydrochloric acid or sirupy citric acid does, showing that the chloral hydrate merely acts as a solvent.

The reagent is conveniently prepared by dissolving 8 grams of chloral hydrate in 5 cc. of water with the addition of 0.5 cc. of concentrated hydrochloric acid.

Endosperm (Figs. 96 and 97, *E*).—A single layer of *aleurone cells*.

Embryo.—The outer layers in cross section are shown in Fig. 96, *C*, and the *epiderm* in surface view in Fig. 97.

CHIEF STRUCTURAL CHARACTERS.—See tables under Seeds of the Mustard Family, Volume I.

Highly characteristic is the carmine color produced in the *palisade cells* on heating with acid chloral hydrate.

CHEMICAL COMPOSITION.—The table below contains analyses of the whole seed by Rothéa² and Grimme³ and of the cake by Rothéa and by Winton and Bornmann.⁴

COMPOSITION OF CHARLOCK SEED AND CAKE

	Water	Protein	Oil, fixed	N-f. ext.	Fiber	Ash
	%	%	%	%	%	%
Charlock seed:						
Rothéa.....	8.14	21.85	25.82	39.49		4.70
Grimme.....	26.7
Charlock cake:						
W. and B.....	9.20	31.19	16.82	26.93	10.44	5.42
Rothéa.....	9.24	27.31	14.34	43.71		5.49

Fixed Fatty Oil. *Physical and Chemical Values*.—Grimme,⁴ Bailey and Burnett,⁵ and Rothéa⁶ have determined the values as shown herewith:

¹ 8th. Int. Cong. Appl. Chem. 1912, 26, 409.

² Bul. sci. pharmcol. 1919, 26, 16.

³ Pharm. Ztg. 1912, 57, 520.

⁴ Loc. cit.

⁵ J. Ind. Eng. Chem. 1916, 8, 429.

⁶ Loc. cit.

VALUES OF CHARLOCK OIL

	Sp. gr. 15.5° C.	Ref. ind. 25° C.	Sapon. No.	Iodine No.	Insol. acids	Liquid Acids		Solid Acids	
					%	%	I No.	%	I No.
B. and B.:									
Expressed oil.	0.9221	1.4734	182.9	121.1	95.3*	89.3	126.0	3.1	...
Ether extract.	0.9272	1.4739	183.1	119.8	95.4*	90.0	122.3	1.6	62.0
Pet. eth. ext..	0.9212	1.4729	181.0	119.3	95.2*	90.0	125.0	2.0	61.0
Grimme:									
Ether extract.	0.9228	1.4720	179.4	102.6	94.2*
Rothéa:									
Expressed oil.	0.9144	177.7	104.9

* Includes unsaponifiable matter. No soluble acids present.

Volatile Oil.—In pure seed furnished by Professors Freeman and Oswald of the University of Minnesota and in seed separated from screenings under a lens Winton and Bornmann¹ found respectively 0.09 and 0.05 per cent of volatile oil. In wild seed separated from wheat screenings they obtained by analysis 0.11 to 0.39 per cent of volatile oil and closely agreeing amounts by calculation based on the percentages of charlock and brown mustard in the samples and the percentages of volatile oil in the pure seeds. Rothéa¹ found in the seed and cake respectively 0.18 and 0.21 per cent of volatile oil but gives no evidence of the purity of the samples.

Phosphorus-Organic Compounds. *Phytin.*—See Indian Mustard.

¹ Loc. cit.

SEEDS OF THE PEA FAMILY

(*Leguminosæ*)

THIS family with so many species yielding bland edible seeds also includes two, tonka bean and fenugreek, with highly aromatic properties.

FENUGREEK

Trigonella Fœnum-Græcum L.

Fr. Fénugrec. Sp. Fenogreco. It. Trigonelle. Ger. Bockshornklee.

Western Asia, Persia, and northern India appear to be the original habitats of fenugreek, but it has long been cultivated throughout the Mediterranean region. Although known chiefly to Europeans as a condiment, the seed is a popular food with the women of north Africa who believe that it produces a well-rounded figure. In the United States it is much used in the preparation of imitation maple flavors. Formerly employed in medicine, fenugreek seed still is added to condition powders and condimental stock feeds, although more for its flavor than for its medicinal or food value. The plant, like others of the family, has value for forage but it is not commonly so used.

MACROSCOPIC STRUCTURE.—*Stem* and trifoliate *leaves* are of the same general structure as those of clovers. Noteworthy characters of the *flower* are the hairy tubular calyx with five narrow teeth and the cream-colored corolla with a short keel. The *pod* is nearly cylindrical, up to 12 mm. long, of which the tapering beak forms about one-third.

The aromatic *seed* (Fig. 98) is usually rounded quadrilateral, up to over 6 mm. long, and on the surface shows clearly the form of the cotyledons and the prominent radicle. In the notch at the end of the radicle is the hilum (with only a trace of accompanying caruncle and cushion) from which a short raphe extends to the chalaza. A cross section shows that, while the bulk of the seed consists of cotyledons, the glassy endosperm is of considerable thickness on the sides of the

cotyledons and also extends between the cotyledon and the radicle. All the parts are more or less brown in color.

MICROSCOPIC STRUCTURE.—Sempolowski¹ deserves special mention among the numerous writers as the first who adequately studied the structure.

Spermoderm (Fig. 99, *S*).—Cross sections bring out the three layers common to most legumes: (1) *palisade cells* (*pal*), up to 85 μ high and 20 μ broad, with a light line (*l*) about 25 μ from the outer end, and a mucilaginous outer membrane into which the more rigid part of each cell is usually extended as a point; (2) *subepiderm* (*sub*) of low (about 20 μ), but relatively broad (70 μ or more), conspicuously ribbed, spool-shaped or truncated-conical cells; and (3) *parenchyma* (*p*), more or less spongy, with no evident differentiation on the inner side into well-defined epidermal cells.

The *palisade cells* are characteristic. Iodine in potassium iodide



FIG. 98.

FIG. 98.—Fenugreek. Seed. $\times 2$. (A.L.W.)

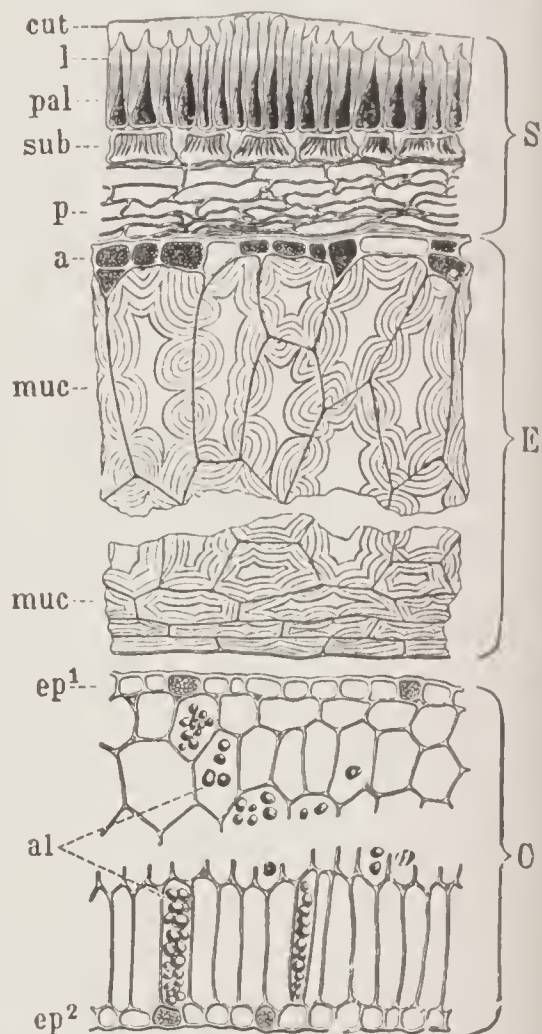


FIG. 99.

FIG. 99.—Fenugreek. Seed in cross section. *S* spermoderm: *pal* palisade cells with *cut* cuticle and *l* light line; *sub* subepiderm; *p* parenchyma. *E* endosperm: *a* aleurone cells; *muc* mucilage cells. *C* cotyledon; *ep*¹ outer epiderm; *ep*² inner epiderm; mesophyl containing *al* aleurone grains. $\times 160$. (A.L.W.)

stains the mucilaginous outer membrane blue; without staining, it is hardly visible. This is considered by some authors to be cuticle, but the true cuticle (*cut*) is an indistinct skin. Not all the cells have points; here and there are groups with flattened outer ends extending to the cuticle.

¹ Landw. Jahrb. 1874, 3, 823.

Caruncle and Hilum Cushion.—Only a very few cells present.

Endosperm (Fig. 99, *E*).—Two distinct tissues make up this coat: (1) *aleurone cells* (*a*), similar to those of the cereals, forming a single, or here and there a double, layer; and (2) *mucilage cells* (*muc*) large and radially elongated in the outer, small and tangentially elongated in the inner, portion.

The *mucilage cells* in water mounts show only very thin middle lamellae, but by special treatment the thick porous mucilaginous secondary walls are evident. For this purpose Tschirch and Oesterle¹ add glycerol slowly to a water mount, whereas Arthur Meyer first hardens the tissue with alcohol, then treats sections with iodine in potassium iodide to which alcohol has been added.

Embryo.—Throughout, the tissues are thin-walled. A triple layer of *palisade cells* underlies the *inner epiderm* (*ep*²) of the cotyledon (Fig. 99, *C*). *Aleurone grains* (*al*), fat, and sometimes a few minute *starch grains* are the visible contents, the former reaching 10 μ in the mesophyl.

CHIEF STRUCTURAL CHARACTERS.—Seed more or less quadrilateral, brown, often 6 mm., with radicle well marked.

Palisade cells up to 85 μ high and 20 μ broad with mucilaginous outer membrane into which the usually pointed walls extend; subepidermal cells spool-shaped, low (20 μ) but broad (70 μ), strongly ribbed; endosperm of aleurone cells and mucilaginous cells; embryo with aleurone grains up to 10 μ .

CHEMICAL COMPOSITION.—A proximate analysis by Wunschen-dorff² shows: water 5.43, protein 28.92, fat 7.36, nitrogen-free extract 42.07 (starch, sugar, mannans, and galactans 40.72), fiber 13.12, and ash 3.00 per cent.

Fleurent,³ who has studied the injurious properties of fenugreek occurring in wheat, reports as follows: water 9.56, soluble protein 1.61, insoluble protein 21.93, fat 8.80, resins 17.42, soluble carbohydrates 9.82, fiber 28.14, soluble ash 1.28, insoluble ash 1.44, and phosphoric acid 0.85 to 0.97 per cent. The resin is stated to melt at 75 to 80° C., contain 5.6 per cent of acids calculated as sulphuric, and dissolve in turpentine. None of the phosphoric acid appeared to exist as phytin.

Proteins.—Wunschendorff⁴ found in fenugreek seed *globulin* 6.8,

¹ Anat. Atlas, Leipzig, 1900, p. 325.

² J. pharm. chim. 1914, 9, 345.

³ Compt. rend. 1927, 184, 1344.

⁴ J. pharm. chim. 1919, 20, 86.

α - and β -albumin 5.4, and nucleoprotein 14.8 per cent. The globulin contains 0.4 per cent of sulphur. The α -albumin coagulates at 60 to 61° C., the β -albumin at 72 to 73° C. Both albumins contain 0.65 per cent of sulphur.

On hydrolysis by heating with hydrochloric acid the nucleoprotein yielded: glycocoll none, alanine 1.6, leucine 7.30, aspartic acid 1.32, glutamic acid 35.71, tyrosine 4.65, phenylalanine 2.50, proline 3.80, tryptophane trace, arginine 3.15, lysine none, and histidine 0.75 per cent. Sugar, purine bases, and pyrimidine bases were not found. The specific rotatory power in alkaline solutions was $-97^{\circ} 7'$.

A prolamin, soluble in hot 70 per cent alcohol but differing from the gliadin of wheat and the zein of maize in that it is insoluble in cold 70 per cent alcohol, has been isolated by Hassan and Basha.¹ Rao, Sastri, and Narayana² note the low content of basic nitrogen and the high content of cystine and tryptophane in the prolamin.

Fat.—According to Wunschendorff³ the oil dissolves readily in ether, benzine, carbon bisulphide, and petroleum ether, but incompletely in acetone. Cold alcohol dissolves 5 per cent of the filtrate. It has marked drying properties, the dried oil being of a golden yellow color and insoluble in ether.

The above author gives the following values: specific gravity at 15° C. 0.9471, refractive index at 25° C. (recalculated) 1.4763, Maumené number 98.9°, saponification number 189.5, iodine number 137.8, solid fatty acids 92.9 per cent, volatile fatty acids 1.50 per cent, acidity 3.20 per cent, unsaponifiable matter 0.9 per cent, phytosterol 0.5 per cent melting at 135.5° C. (acetate 131°), and lecithin 6.25 per cent.

The fatty acids consist largely of linoleic and palmitic together with much smaller amounts of linoleic and oleic acids.

Fleurent⁴ states that the seed contains 9.46 to 9.85 per cent of oil having a specific gravity at 15° C. (recalculated) of 0.972 and an iodine number of 110 to 114. He further states that the disagreeable odor is due to the oil and the bitter taste to the alcohol-soluble resin. Bread made from flour containing as little as 6 milligrams of fenugreek oil and 8 milligrams of fenugreek resin per 100 grams, although edible, is lacking in agreeable flavor.

Wunschendorff⁵ notes that the offensive odor passes through the

¹ Biochem J. 1932, **26**, 1843.

² J. Indian Inst. Sci. 1933, **16A**, 85.

³ J. pharm. chim. 1919, **19**, 397.

⁴ Compt. rend. 1926, **182**, 944.

⁵ J. pharm. chim. 1914, **10**, 152.

body into the perspiration. He found neither the odor nor the bitter taste in the fresh seed, hence he concludes that they are formed during drying by the action of enzymes. Treatment of the fresh seed with the vapor of boiling alcohol prevents their formation.

Volatile Oil.—Little is known of the volatile oil of fenugreek. Its specific gravity is stated to be 0.871 at 15.5° C.

Carbohydrates.—Iyer and Sastri¹ isolated a *mucilage* which they identified as a manno-galactan.

Phosphorus-Organic Compounds.—In fenugreek flour containing 36 per cent of protein Wunschendorff² found 1.042 per cent of total phosphoric acid (P_2O_5) of which 0.758 per cent existed as *phytin*, 0.149 per cent as *nucleoalbumin*, and 0.135 per cent as *lecithin*. The total phosphoric acid reported in the flour is over twice that found in the ash analysis, indicating either a loss in burning in the latter case or else that the 11.43 per cent of "undetermined" belonged in large part with the phosphoric acid.

The *lipins* named by Sastri and Sreenivasaya³ in a preliminary report are: (1) a phospholipin related to sphingomyelin, (2) an oil-soluble true lecithin, (3) a pyridine-soluble galactolipin, (4) a galactoside, and (5) a pyridine-insoluble galactolipin containing sulphur.

Enzymes.—Bourquelot and Hérissé⁴ discovered a soluble ferment, *seminase*, secreted by the embryo during fermentation, which hydrolyzes the cell wall carbohydrates to mannose and galactose.

Mineral Constituents.—An analysis of the sample in which Wunschendorff determined the proximate constituents yielded: potash 33.77, soda 5.30, lime 8.37, magnesia 7.12, ferric oxide 2.20, manganic oxide trace, phosphoric acid 14.19, sulphuric acid 7.09, chlorine 5.81, silica 4.76, and undetermined 11.43 per cent.

Minor Mineral Constituents. *Manganese.*—Air-dry basis, 14.5 mg. per kilo, (Quartaroli).⁵

Copper.—Air-dry basis, 16.25 mg. per kilo (Quartaroli).⁵

¹ J. Indian Inst. Sci. 1933, **16A**, 88.

² J. pharm. chim. 1914, **10**, 152.

³ Proc. Indian Acad. Sci. 1936, **3A**, 513.

⁴ Compt. rend. 1900, **130**, 731.

⁵ Ann. chim, appl, 1928, **18**, 47.

TONKA BEAN

Coumarouna odorata Aubl. = *Dipteryx odorata* Willd.

Fr. Fève tonka. Sp. Haba tonca. Ger. Tonkabohne.

A tree growing in the northern countries of South America yields the highly aromatic seed known as the tonka or tonquin bean. The world's supply comes chiefly from Venezuela, Guiana, and the province of Para in Brazil.

Since the tonka bean is classed with foods solely because of its flavoring property it is considered in this chapter rather than with common legumes which rank as vegetables or feeds. This separation is no serious objection in studying the comparative histology of the leguminous seeds as the tree is the sole representative of the *Dalbergia* group yielding a food and the structure of the seed is quite unlike that of other common members of the family.

The smallest quantity of the seed is made evident by its peculiar fragrance suggesting vanilla, although much ranker. The flavoring principle coumarin bears chemically no relation to vanillin, the chief principle of the vanilla bean. As is true also of vanillin, coumarin is prepared synthetically, and this artificial substance has to a considerable extent replaced the natural as an ingredient of foods as well as of cordials, medicines, snuff, and perfumery.

So-called "English tonka beans," the seeds of *C. oppositifolia* Willd., are smaller than those of common or Dutch tonka beans, but otherwise similar.

Coumarin also occurs in sweet vernal or vanilla grass (*Anthoxanthum odoratum*) used for basket work, in various species of sweet clover (*Melilotus*), and in sweet woodruff (*Asperula odorata*), known in Teutonic countries as *Waldmeister* and used there in the much-esteemed punch known as "Maibowle."

MACROSCOPIC STRUCTURE.—The flowers are borne in terminal racemes. Two of the calyx lobes are large and winglike; the other three are reduced to inconspicuous teeth. The pealike corolla is rose or purple. The stamens are monadelphous. Only one ovule is present in the stalked ovary, the latter developing into a drupelike pod with a woody endocarp in which the seed is suspended, the hilum being at the convex edge near one end. In the dried form (Fig. 100) as found in commerce, the seed is elongated, up to 5 cm., somewhat flattened. Both the thin brittle dark brown skins (spermoderm with adhering endosperm) and the light brown cotyledons are wrinkled on the sur-

face. The cotyledons constitute the bulk of the seed; the radicle is short.

MICROSCOPIC STRUCTURE.—Several authors, notably Hanaušek in the three editions of Wiesner's *Rohstoffe des Pflanzenreiches*, describe the tissues.

Spermoderm (Fig. 101, *S*).—Although the structure conforms in general to that of legumes used as vegetables, both the palisade cells and the subepidermal cells have characters peculiar to the genus. The



FIG. 100.

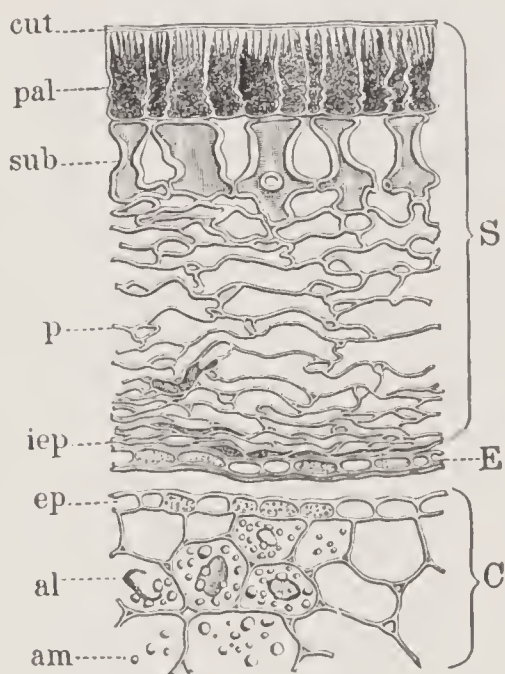


FIG. 101.

FIG. 100.—Tonka Bean. Seed. $\times 1$. (A.L.W.)

FIG. 101.—Tonka Bean. Seed in cross section. *S* spermoderm: *pal* palisade cells with *cut* cuticle; *sub* subepidermis; *p* spongy parenchyma; *iep* inner epidermis. *E* endosperm. *C* cotyledon: *ep* outer epidermis; mesophyll with *al* aleurone grains and *am* starch grains. $\times 160$. (K.B.W.)

four tissues are: (1) *palisade cells* (*pal*), up to $60\ \mu$ high and $25\ \mu$ broad, with a thin cuticle and thin walls except toward the outer end where they are ribbed; (2) *subepidermal cells* (*sub*), about $60\ \mu$ high and $50\ \mu$ broad, irregularly spool-shaped, with inner portion forming part of the spongy parenchyma of the next layer; (3) *spongy parenchyma* (*p*) of cells more or less star-shaped in surface view; and (4) *inner epidermis* (*iep*) of somewhat tangentially elongated cells.

The *palisade cells* are strikingly different from those of garden legumes but somewhat resemble those of the peanut. All the tissues have more or less dark contents.

Endosperm (Fig. 101, *E*).—A typical *aleurone layer*, which Hanausek considers to be perisperm, and a layer of *compressed cells* form the thin endosperm.

Embryo.—*Aleurone grains* are present throughout the tissues, those in the longitudinally elongated cells of the *epiderms* (*ep*) of the cotyledon (Fig. 101, *C*) being small and the only contents of a definite form. In the isodiametric *mesophyl* cells the aleurone grains reach $35\ \mu$. Some *starch grains*, up to $10\ \mu$, may also be present in the fatty matrix. Both aleurone and starch grains are best seen after extraction with a fat solvent and staining with iodine in potassium iodide. Hanausek notes that preliminary treatment with alcohol renders the starch grains nearly inert to the iodine solution owing as he believes to the formation of a protective coating.

Whether the so-called aleurone grains are true to name is questionable as they do not appear to contain either globoids or crystalloids. Quite possibly they are merely protein concretions.

CHIEF STRUCTURAL CHARACTERS.—Seed dark colored throughout with characteristic odor.

Palisade cells broad and thin-walled in inner part, ribbed in outer part; subepidermal cells irregularly spool-shaped, confluent with parenchyma; endosperm of one cell layer of aleurone cells and compressed inner cells; cotyledon with aleurone grains up to $35\ \mu$ and sometimes starch grains up to $10\ \mu$.

CHEMICAL COMPOSITION.—The composition of the tonka bean has been studied chiefly as regards its content of coumarin and fat. The kinds and amounts of proteins and carbohydrates are subjects for future investigation.

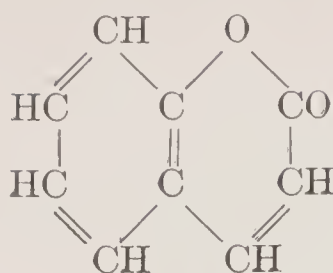
Tonka Extract.—See Vanilla Extract.

Fat.—The content of fat is about 25 per cent. Under the name "tonka butter" the expressed fat is used in the West Indies for culinary purposes. The following values obtained by Duyk¹ indicate chemical relationship with the cocoanut oil group: specific gravity at 100°C . 0.888, refractive index (40° ?) 1.4572, saponification number 257, Reichert-Meissl number 5.4, and ester number 250. The following values by Georgi and Teik,² however, indicate a different composition: specific gravity at $99^{\circ}/15.5^{\circ}$ 0.878, refractive index at 27°C . 1.4680, melting point 7.2 to 11.8° , saponification number 198.5, iodine number (Wijs) 72.6, acid number 1.0, and unsaponifiable matter 0.5 per cent.

Coumarin, $\text{C}_9\text{H}_6\text{O}_2$, is the anhydride of coumaric acid.

¹ Rep. pharm. 1908, **20** [3], 193.

² J. Soc. Chem. Ind. 1931, **50**, 318T.



Coumarin

The results of analyses of the 1:10 extract such as given under vanilla show that the coumarin content of the bean reaches or exceeds about 3 per cent. Coumarin may be prepared from the alcoholic extract of the tonka bean or sweet woodruff or else synthetically by warming sodium salicylaldehyde with acetic anhydride, the acetocumaric acid first formed splitting up into coumarin and acetic acid. The substance forms colorless crystalline scales, melting at 67° C., and boiling at 290° C., readily soluble in alcohol and ether, but only slightly so in cold water. Heated with aqueous potash lye it decomposes with formation of coumaric acid, but fused with dry potassium hydroxide it splits up into salicylic and acetic acids.

FRUITS OF THE NASTURTIUM FAMILY

(*Tropæolaceæ*)

GREEN fruits of this family are of minor importance for flavoring.

NASTURTIUM

Tropæolum majus L. and *T. minus* L.

Fr. Capucine. Sp. Nastureio. It. Nasturzio. Ger. Kapuzinerkresse.

Both species, natives of South America, are favorite garden flowers with a wide range of color.

The flowers are acceptable additions to salads; the flower buds and green fruit "seeds" are pickled and used as substitutes for capers.

MACROSCOPIC STRUCTURE.—The three-lobed *fruit* separates into three ovoid one-seeded carpels, about 1 cm. long, with several grooves on the back, each forming a snail-like spiral. The straight embryo of the anatropous *seed* has plano-convex cotyledons.

MICROSCOPIC STRUCTURE.—At the green stage, when suitable for pickling, most of the tissues are characterless.

Pericarp.—The *epicarp* of polygonal cells has a striated cuticle. The *mesocarp* cells are porous.

Spermoderm.—Usually about ten cells thick, thin-walled, characterless.

Cotyledons.—When of sufficient maturity the cell walls are thickened, porous, becoming blue with iodine in potassium iodide.

CHIEF STRUCTURAL CHARACTERS.—Carpel ovoid, grooved, one-seeded.

Epicarp striated. Cotyledon cells with thickened walls, blue with iodine in potassium iodide.

FRUITS OF THE RUE FAMILY

(*Rutaceæ*)

THE general structure and composition of the fruits of this family are described in Volume II under Fruits. Only the characters and composition of the volatile oil are given herewith.

SWEET ORANGE

Citrus sinensis Osbeck = *C. Aurantium* var. *sinensis* L. = *C. Aurantium* Risso

Fr. Orange douce. Sp. Naranja. It. Arancio dolce. Ger. Apfelsine.

Sweet Orange Oil. *Physical and Chemical Values.*—The composition of Sicilian orange oils is well illustrated by the analyses (not published at the time) of 28 samples collected by Chace¹ during the years 1907 to 1909 at factories, for the most part from bowls of workmen. Analyses on essentially the same plan were made by Poore¹ of 63 samples of oils from Valencia fruit, picked from April to November, and of 31 samples of oils from Washington Navel fruit, picked from November to May, obtained in both cases from an orange by-products company during the years 1923 to 1926 inclusive. A comparison of the following summaries with the results of other analysts, notably Schimmel & Co.,² Berté and Romeo,³ Berté,⁴ Romeo,⁵ De Villiers,⁶ Chiris,⁷ and Naves,⁸ shows that the limits for the several values may be accepted as applying to orange oils in general.

The solubility in 90 per cent alcohol ranges from 4 to 20 volumes and in 95 per cent alcohol from 0.5 to 5.0 volumes.

¹ U. S. Dept. Agr. 1932, Tech. Bul. 241.

² Rep. 1897, 22.

³ Publication issued by Messina Chamber of Commerce before the earthquake; abstracted in Chem. Abs. 1909, 3, 1058.

⁴ Riv. ital. ess. Profum. 1922, 4, 2; 1931, 13, 75.

⁵ Ibid. 1923, 5, 15.

⁶ Farm. in S. Africa 1930, 4, 515.

⁷ Parf. France 1930, 8, 166.

⁸ Ibid. 1932, 10, 160.

VALUES OF ORANGE OIL

	Sp. gr. 15.5° C.*	Solids	Ref. ind. 20° C.		Opt. rot. 20° C.		Alde- hydes†	Es- ters
			Direct	10% Dist.	Direct	10% Dist.		
		%	°	°	°	°	%	%
Sicilian (Chace)								
Min.	0.8473	1.4723	1.4710	+92.03	+95.90	1.47‡	...
Max.	0.8530	1.4737	1.4723	+99.60	+99.40	2.89‡	...
Aver.	0.8498	1.4729	1.4716	+98.50	+98.45	2.12‡	...
Calif. (Poore)								
Valencia:								
Min.	0.8467	1.93	1.4728	1.4718	+95.71	+97.94	0.8	0.44
Max.	0.8536	6.26	1.4746	1.4727	+99.58	+100.44	2.2	1.76
Aver.	0.8494	3.61	1.4735	1.4723	+97.78	+99.21	1.4	0.83
Wash. Navel:								
Min.	0.8473	1.49	1.4731	1.4721	+94.18	+97.51	0.6	0.49
Max.	0.8557	8.17	1.4748	1.4727	+99.32	+99.59	1.0	2.58
Aver.	0.8509	4.53	1.4738	1.4724	+96.93	+98.71	0.8	1.38

* Recalculated from 25° C. † Determined by Kleber method; calculated as citral although largely decyl aldehyde. ‡ 22 samples.

The *U. S. Standards* require that orange oil have an optical rotation at 25° C. of not less than +95°. They designate the species as *C. aurantium* L. which is the bitter orange, notwithstanding the fact that the orange oil used for making orange extract is commonly from the sweet orange (*C. sinensis* Osbeck = *C. Aurantium* var. *sinensis* L.). The standards further require that orange extract contain 5 per cent of orange oil.

Spanish sweet orange oil, made by a new (extraction?) process, gave in the hands of Tedesko¹ specific gravity at 15° C. 0.8576; optical rotation at 20° C. + 92.4, decyl aldehyde (Kleber) 2.3 per cent, non-volatile residue 8.9 per cent, ester number of residue 96.3, acid number of residue 20.1, ester number of oil less ester number of residue 11.0, and esters as linalyl acetate 3.1 per cent.

The somewhat meager results available, such as by Dowzard,² Berté and Romeo,³ and Schimmel & Co.,⁴ appear to indicate that oil

¹ *Parf. mod.* 1927, 20, 44.

² *Am. J. Pharm.* 1908, 80, 474.

³ *Loc. cit.*

⁴ *Rep.* Oct. 1914/Apr. 1915.

of bitter orange is a trifle higher in specific gravity and lower in optical rotation and aldehydes than oil of sweet orange, but this has been disputed.

Constituents.—Wallach ¹ estimates that *d-limonene* forms about 90 per cent of both orange and lemon oil, and Poore ² accepts that estimate. Other terpenes occur in very small amount, if at all, and pinene appears to be absent. Parry ³ and Gildemeister and Hoffmann ⁴ question the presence of *citral* reported by Semmler, ⁵ but Nelson and Mottern ⁶ have shown that it occurs in Florida Valencia orange oil. The presence of *decyl aldehyde* was first announced by Stephan ⁷ and confirmed by Poore. ² *Methyl anthranilate*, isolated by Parry ⁸ and later by Schimmel & Co., ⁹ contributes to the delightful and characteristic odor. Parry also found *d-linalool*, *d-terpineol*, *nonylic alcohol*, and an ester of caprylic acid. *Octyl* and *decyl alcohols* have been detected in small amount. Poore mentions *formic*, *acetic*, *capric*, and *caprylic acids*. Naves ¹⁰ found in decomposed orange oil *dl-carvone*, *formaldehyde*, and a trace of a *saturated ketonic compound*.

Decyl Aldehyde, $C_{10}H_{20}O$ or $CH_3(CH_2)_8 \cdot CHO$, given by Schimmel & Co. ¹¹ as an important odorous constituent of the volatile oil of orange, neroli, and cassia buds, is a liquid with specific gravity at 15° C. 0.828, refractive index at 22° C. 1.4273, and boiling point at 755 mm. 209° C. It is optically inactive.

Orange Flower or Neroli Oil, a well-known perfume and flavor for liqueurs, contains most of the constituents present in orange oil but in different proportions, also others.

Its *Physical and Chemical Values* are: specific gravity at 15° C. 0.831 to 0.924, refractive index at 20° C. 1.4680 to 1.4748, optical rotation -2.5 to $+10^\circ$, and esters as linalyl acetate 9 to 24 per cent. It is soluble in 1 to 2 volumes of 80 per cent alcohol.

¹ Ann. 1885, 227, 227.

² Loc. cit.

³ Allen: Com'l. Org. Anal. 1917, 9, 368.

⁴ Ätherischen Öle, 3 Aufl. 1931, 3, 83.

⁵ Ber. 1891, 24, 202.

⁶ J. Am. Chem. Soc. 1934, 56, 1238.

⁷ J. prakt. Chem. 1900, [II], 62, 523.

⁸ Chem. Drug. 1900, 56, 462, 721.

⁹ Rep. Apr. 1900, 21.

¹⁰ Parf. France 1932, 10, 225.

¹¹ Rep. Oct. 1900, 45; Oct. 1902, 55; Oct. 1903, 49.

Constituents.—Tiemann and Semmler¹ isolated *limonene*, *linalyl acetate* (up to 18 per cent), *l-linalool* (up to 25 per cent), and *geraniol*. Schimmel & Co.² found *methyl anthranilate*, also the terpenes *dipentene*, *l- α -pinene*, and *l-camphene*, *decyl aldehyde*, *phenyl-ethyl alcohol*, *α -terpineol*, *farnesol*, *acetic acid*, *phenyl acetic acid*, *benzoic acid*, and so-called *aurade* or *neroli camphor*. Hesse and Zeitschel³ added to the list *nerolidol* ($C_{15}H_{26}O$), a sesquiterpene alcohol; *nerol*, an isomer of *geraniol*; *acetic* and *palmitic acids*, the former partly combined with *nerol* and *geraniol*; and traces of *indol*.

Bergamot Oil, obtained by pressure from *C. bergamia* Risso, is much used in perfumes and medicines, but is not adapted as a food flavor.

Physical and Chemical Values.—The oil is of interest, because it differs from orange oil in that it contains in addition to *d-limonene*, 35 to 45 per cent of the odorous liquid substance *l-linalyl acetate*, the non-odorous crystalline substance *bergaptene* ($C_{12}H_{18}O$), shown by Pomeranz to be the methyl ester of dioxycoumarin. The following, except the refractive index, are based on results by Berté and Romeo⁴ and LaFace:⁵ specific gravity at 15° C. 0.879 to 0.890, refractive index at 20° C. 1.464 to 1.469 (Parry), optical rotation +7 to +32°, and esters as *linalyl acetate* 33 to 49 per cent.

Constituents.—*Linalyl acetate*, $C_{12}H_{20}O_2$ or $C_{10}H_{17}O \cdot OC \cdot CH_3$, is a liquid with the odor of bergamot; specific gravity at 15° C. 0.898; boiling point under 10 mm. pressure 100 to 102° C. It has been isolated as a dextro or levorotatory modification from bergamot, orange flowers, sassafras, and other oils.

Other constituents identified by Burgess and Page⁶ are *α -pinene*, *camphene*, *bisabolene* (limene), and *acetic acid*, and by Elze,⁷ *dihydrocuminic alcohol*, *nerol*, and *terpineol*.

¹ Ber. 1893, 26, 2708.

² Rep. Oct. 1902, 54; 1914, 72.

³ J. prakt. Chem. 1902, 66, 481, 516.

⁴ Loc. cit.

⁵ Rev. ital. ess. prof. 1923, 5, 65.

⁶ J. Chem. Soc. 1904, 85, 1327.

⁷ Chem. Ztg. 1910, 34, 538.

MANDARIN ORANGE AND TANGERINE

Citrus nobilis Lour. var. *deliciosa* Swingle

Mandarin Oil. *Physical and Chemical Values.*—According to analyses by Schimmel & Co.,¹ Parry,² and others, the oil has a range in values similar to that of orange oil, namely specific gravity at 15° C. 0.850 to 0.860 and optical rotation +65 to +75°.

Constituents.—*Tangeretin*, $C_{15}H_5O_2(OCH_3)_5$, the first natural fully methylated flavanol reported, discovered and named by Nelson,³ separates out from expressed tangerine oil on long standing in a refrigerator. It forms colorless, double, extremely refractive rods and needles melting at 154° C. (corrected).

LEMON

Citrus Limonia Osbeck = *C. Medica* var. *Limon* L. = *C. Limonium* Risso.

Fr. Citron. Sp. Limón. It. Limone. Ger. Limone.

The structure of the fruit and the composition of the parts and the products made therefrom, other than the volatile oil, are treated in Volume II.

Lemon Oil of standard quality is an expressed product, not like most essential oils a distillation product. In Sicily, the chief European region of production, the lemon skin is soaked in water and the oil pressed out with the hands into a sponge from which it is removed by squeezing and then clarified. The small amount remaining in the skin is reclaimed by distillation. On the mainland of Italy crude machines and in Florida and California machines of modern construction are used. Usually the manufacture of calcium citrate, the first step in the manufacture of citric acid, goes hand in hand with that of the oil.

Physical and Chemical Values.—Chace⁴ analyzed 195 samples of Sicilian lemon oil, collected during 1907 and 1909 at factories for the most part from bowls of workmen. Following essentially the same methods, Poore⁵ analyzed 73 samples of California oils furnished by

¹ Reports from 1894 to 1895.

² Chem. and Drug. 1899, I, 53, 420.

³ J. Am. Chem. Soc. 1934, 56, 1392.

⁴ U. S. Dept. Agr., Bur. Chem. 1910, Circ. 46.

⁵ U. S. Dept. Agr. 1932, Tech. Bul. 241.

a by-products company during 1923 to 1926. The notable difference in the products of the two regions was the lower citral content of the California oils and the lower specific gravity of the Sicilian oils.

VALUES OF SICILIAN AND CALIFORNIA LEMON OIL

	Sp. gr. 15.5° C.*	Solids	Ref. ind. 20° C.		Opt. rot. 20° C.		Citral		Esters
			Direct	10% Dist.	Direct	10% Dist.	Kleber	Hiltner	
		%	°	°	°	°	%	%	%
Sicilian (Chace):									
Min.....	0.8503	1.4740	1.4720	+54.16	+49.08	3.4†	2.6†
Max.....	0.8552	1.4758	1.4735	+66.28	+63.98	5.2†	5.3†
Aver.....	0.8522	1.4748	1.4726	+60.12	+56.64	4.5†	4.2†
Calif. (Poore):									
Min.....	0.8529	2.01	1.4738	1.4726	+52.71	+46.47	2.0	1.4	1.76
Max.....	0.8579	4.52	1.4749	1.4737	+70.18	+65.74	3.7	3.7	3.12
Aver.....	0.8551	2.96	1.4743	1.4730	+62.48	+57.90	2.8	2.3	2.38

* Recalculated from 25° C. † 50 samples.

The *U. S. Standards* require that lemon oil have an optical rotation at 25° C. of not less than +60° and contain not less than 4 per cent by weight of citral, also that lemon extract contain not less than 5 per cent by volume of lemon oil, and terpeneless lemon extract not less than 0.2 per cent by weight of citral.

Other analysts reporting figures on refractive index and optical rotation of Italian (Sicilian, Calabrian, etc.) oils, showing practically the same range as those of Chace here summarized, are Burgess and Child,¹ Berté and Romeo, publishing together and separately (see *Orange Oil*), Schimmel & Co.,² Romeo,³ Liotta,⁴ and Ogston and Moore,⁵ but their figures on specific gravity are higher, the range being from 0.854 to 0.864, and on citral reaching in some cases 7.5 per cent, although the trend in recent years has been downward.

Parry,⁶ in Australian oil, obtained specific gravity 0.8558, solids 1.09 per cent, refractive index 1.4736, optical rotation +62°, and citral 3.5 per cent.

The solubility in 80 per cent alcohol is variously stated as 1 to 2 volumes.

¹ J. Soc. Chem. Ind. 1901, 20, 1176.

² Rep. Oct. 1896, 38; Oct. 1897, 22; Apr. May 1901, 27.

³ Riv. ital. ess. profum. 1923, 5, 15.

⁴ Profum. ital. 1925, 3, 340.

⁵ Perf. ess. Oil Rec. 1925, 16, 114.

⁶ Ibid. 1924, 15, 250.

Constituents.—The chief constituent is the terpene *d-limonene* or dipentene (see formula, Introduction to Part III), forming, as first shown by Wallach,¹ about 90 per cent of the oil. Other terpenes present in small amount are β -*phellandrene* and γ -*terpinene*, isolated by Gildemeister and Müller,² and *l-camphene*, isolated by Burgess and Child.³ The last-named authors⁴ and Schimmel & Co. identified *l*- β -, *l*- α -, and *i*- α -*pinene* and *sesquiterpenes*. Poore⁵ mentions the sesquiterpene *bisabolene*. Chace⁶ considers that the presence of more than traces of pinene, as shown by his nitrosochloride test, is indicative of the presence of foreign oils.

Of the oxygenated substances, *citral* leads both in amount and in fragrance. Other aldehydes stated to be present in small amount are *citronellal*, announced by Doebner,⁷ but not generally credited, *octylaldehyde*, and *nonylaldehyde*, both reported by Von Soden and Rojahn.⁸ *Geranyl* and *linalyl acetates* were found by Umney and Swinton,⁹ *terpineol* and *methyl heptenone* by Schimmel & Co.¹⁰ Poore⁵ states that *acetic*, *capric*, and *caprylic acids* are present.

From the non-volatile portion Schmidt¹¹ isolated *citroptene*, $C_{11}H_{10}O_4$ or $C_6H_2(OCH_3)_2$ $(CH : CH \cdot \underset{|}{\underset{|}{CO}})(O)$, melting at $146^\circ C.$, and Romeo,¹² bitter but odorless dextrorotatory crystals ($C_{10}H_{18}O_2$), melting at $58^\circ C.$, of unknown structure.

Limonene, $C_{10}H_{16}$ (see structural formula in Introduction to Part III), exists in two modifications with opposite polarizations, *d*- and *l*-*limonene*. On mixing equal parts of the two forms, the racemic form (*dipentene*) is obtained, which is also formed on heating either the *d*- or *l*-*limonene*. Other names for limonene are *citrene*, *carvene*, and *hesperidene*. The *d*-form is the chief constituent of several citrous oils, notably lemon oil. Its specific gravity at $15.5^\circ C.$ is 0.847, its boiling point $175^\circ C.$, and its optical rotation α_D is $+106.8^\circ$.

Citral or *geranial*, $C_{10}H_{16}O$ (see structural formula in Introduc-

¹ Ann. 1885, 227, 277.

² Schimmel & Co. Rep. 1897, 96; 1909, 63.

³ Chem. Drug. 1903, 62, 476.

⁴ J. Soc. Chem. Ind. 1901, 20, 1176.

⁵ U. S. Dept. Agr. 1932, Tech. Bul. 241.

⁶ Loc. cit.

⁷ Arch. Pharm. 1894, 232, 688.

⁸ Ber. 1901, 34, 2809.

⁹ Pharm. J. 1898, 7, 196, 370.

¹⁰ Rep. Oct. 1902, 39.

¹¹ Arch. Pharm. 1904, 242, 288.

¹² Ann. chim. appl. 1925, 15, 305.

tion to Part III), an aldehyde, unlike limonene is soluble in dilute alcohol, thus permitting the manufacture of a cheaper flavoring solution than one prepared by the solution of lemon oil in strong alcohol. It has the fragrance of lemon oil, but lacks the body that limonene imparts to an extract.

Semmler obtained citral synthetically by oxidizing geranial with chromic acid. Tiemann prepared *a*- and *b*-forms depending on the position of the CHO group. The properties follow: specific gravity at 15.5° C. 0.893 to 0.897, boiling point 224 to 229° C. with partial decomposition (at 12 mm. 112° without change), and refractive index at 20° C. 1.489 to 1.490. The range given is sufficiently wide to include *a*- and *b*-forms. When pure it is optically inactive. On heating at 170° C. with potassium bisulphide, cymol is formed. Hiltner¹ employs the yellow color formed with metaphenylene diamine hydrochloride for its colorimetric determination. Kleber titrates with acid a standard solution of phenylhydrazine before and after addition of a weighed portion of the sample.

Terpeneless Lemon Oil.—Romeo² describes two kinds: the first is prepared with removal of only the diterpene; the second with removal of both the di- and sesquiterpenes, the values of the two being: specific gravity at 15° C. 0.8935 to 0.8990, 0.898 to 0.992; optical rotation -8.3 to -5° , -3.7 to $+1^\circ$; citral 40 to 52, about 65 per cent; and soluble in alcohol 1 to 2 volumes of 80 per cent, 1 to 3 volumes of 70 per cent.

LIME

Citrus aurantifolia Swingle = *C. limetta* Auct. = *Limonia aurantifolia* Christ.

Fr. Lime. Sp. Lima. Ger. Lime.

The structure and composition of the fruits are given in Volume II.

Lime Oil. *Physical and Chemical Values.*—Parry³ in an experimental lot of distilled lime oil from Nigeria found: specific gravity 0.882, refractive index at 20° C. 1.4775, and optical rotation $+34^\circ$. A later report by the same author⁴ gives the range of French and English oils as: specific gravity 0.868 to 0.879, refractive index 1.4768

¹ J. Ind. Eng. Chem. 1909, **1**, 798; 1918, **10**, 608.

² Atti cong. naz. chim. pura appl. 1923, p. 326.

³ Perf. Ess. Oil Rec. 1918, **9**, 31.

⁴ Perf. mod. 1926, **19**, 97.

to 1.4798, and optical rotation $+40$ to $+46^\circ$. Schimmel & Co.¹ give $+50^\circ$ as the optical rotation of an Italian oil.

Constituents.—Gildemeister² names *d-limonene*, *linaloöl*, and *l-linalyl acetate* (26 per cent) as constituents of the expressed Italian oil. Data on West Indian oil are meager.

GRAPEFRUIT

C. grandis Osbeck = *C. Aurantium* var. *grandis* L. = *C. decumana* L.

Fr. Pompelmouse. It. Pomo di paradiso. Ger. Pompelmus.

The structure and general composition of the fruit are treated in Volume II.

Grapefruit Oil.—Distilled oil, as examined by Zoller,³ gave: specific gravity at 20° C. 0.845 to 0.860; refractive index 1.4950 to 1.4785; optical rotation $+72.5$ to $+78.5^\circ$; *d-limonene* 90 to 92 per cent; citral 3 to 5 per cent; *d-pinene* 0.5 to 1.5 per cent; and linaloöl 1 to 2 per cent. Results by Chiris⁴ on distilled and expressed oils are: specific gravity at 15° C. 0.853, —; refractive index at 20° C. 1.4737, 1.4744; optical rotation at 20° C. $+95.5^\circ$, $+90.5^\circ$; soluble in 95 per cent alcohol 2.5 volumes or more, 20 volumes with slight turbidity.

Constituents.—Florida grapefruit peel oil, with average specific gravity at 20° C. 0.8563, refractive index at 20° C. 1.4758, optical rotation at 20° C. $+93.28^\circ$, and aldehyde content as octyl and decyl 1.67 per cent, was found by Nelson and Mottern⁵ to consist approximately of 90 per cent of *limonene*, 2 to 3 per cent of *oxygenated volatile constituents* and *sesquiterpenes*, 7 to 8 per cent of *waxy materials*, and smaller amounts of *octyl* and *decyl aldehydes*, *geraniol* and *octyl alcohol* (both free and as acetates), *cadinene*, *citral*, and *methyl anthranilate*.

¹ Schimmel & Co. Ber. Apr. 1897, table 28.

² Arch. Pharm. 1895, **233**, 175.

³ Oil, Paint Drug Rep. 1918, **94**, 72B.

⁴ Parf. France 1930, **8**, 166.

⁵ Ind. Eng. Chem. 1934, **26**, 634.

FRUITS OF THE MYRTLE FAMILY

(*Myrtaceæ*)

IN addition to cloves, a flower bud, allspice, a fruit spice, belongs in this family.

ALLSPICE

Pimenta officinalis Berg = *Myrtus Pimenta* L. = *Eugenia Pimenta* DC.

Fr. Piment de la Jamaïque. Sp. Pimento. It. Coccòla di pimento. Ger. Piment.

While most of the common spices are natives of the East Indies, the allspice or pimento tree originated in the West Indies. In Jamaica it grows abundantly both wild and under cultivation. The name allspice refers to the flavor, which is supposed to resemble a combination of cloves, nutmeg, and cinnamon.

The fruit is picked when nearly or quite fully formed, but still green, the flavor being best at this stage. Formerly ground cocoanut shell was a common adulterant of the ground spice.

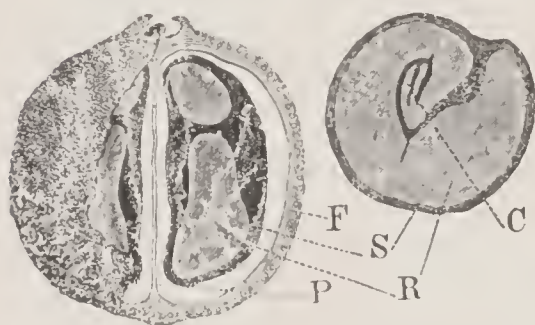


FIG. 102.—Allspice. Left: fruit and seed in longitudinal section. Right: seed in cross section. *F* pericarp; *P* partition; *S* spermoderm; *R* radicle; *C* cotyledons. $\times 4$. (A.L.W.)

Bayberry or crown allspice (*P. acris* Kostel, also variously assigned to the genera *Myrcia*, *Myrtus*, and *Amomis*) has an oblong fruit up to 10 mm., with a spicy taste. The leaves distilled with rum yield bay rum, the well-known toilet preparation and hair tonic.

Mexican or Tabasco allspice (*Eugenia Tabasco* G. Don) is a large-fruited species regarded by some as a variety of true allspice.

MACROSCOPIC STRUCTURE.—The flowers are small, white, with four calyx lobes, four petals, and numerous stamens, borne on a top-shaped, usually two-celled and two-loculed ovary, or rather consolidated receptacle and ovary. The berries (Fig. 102) are medium

brown, warty, globular up to 8 mm., and crowned with the four minute calyx lobes. Normally there are two dark brown campylotropous, pendulous seeds, convex and roughened on the outer side, flattened and smooth on the inner. Sometimes, as in the case of pea berry coffee, only a single globular seed develops; on the other hand there may be three seeds. Unlike that of mother cloves and the species of *Eugenia* yielding table fruits, the embryo is spiral with strongly developed radicle (*R*) but minute cotyledons (*C*). The partition (*P*) between the two locules is thin, papery, of a light buff color.

MICROSCOPIC STRUCTURE.—Most of the writers on the histology of drugs and foods describe allspice.

Receptacle and Pericarp (Figs. 103 and 105).—Owing to the dark coloring matter, extraction of sections with alco-

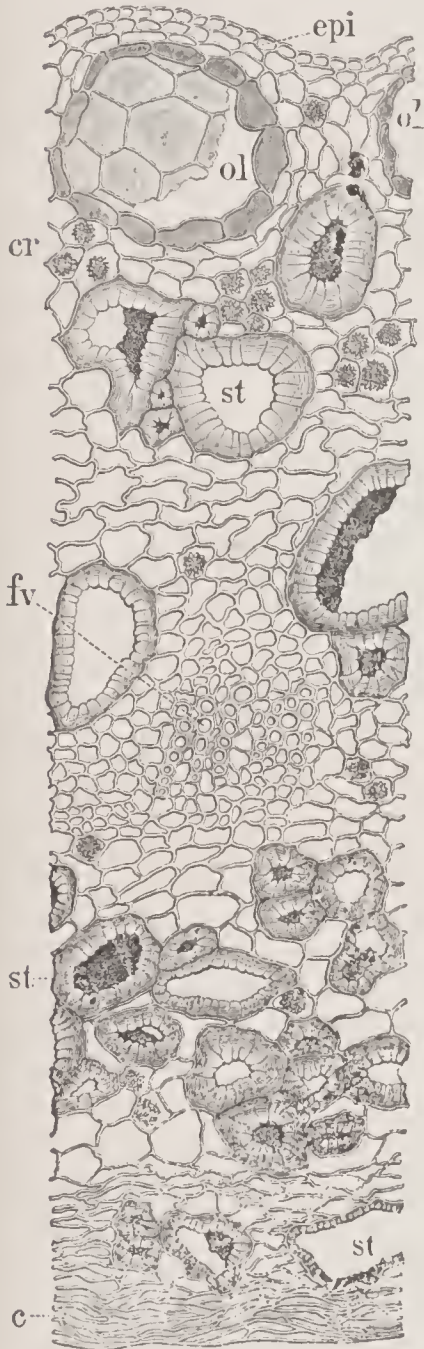


FIG. 103.

FIG. 103.—Allspice. Pericarp in cross section. *epi* epicarp; *ol* volatile oil cavities; *cr* crystal rosettes; *fv* bundle; *st* stone cells; *c* compressed cells of inner parenchyma. $\times 160$. (A.L.W.)

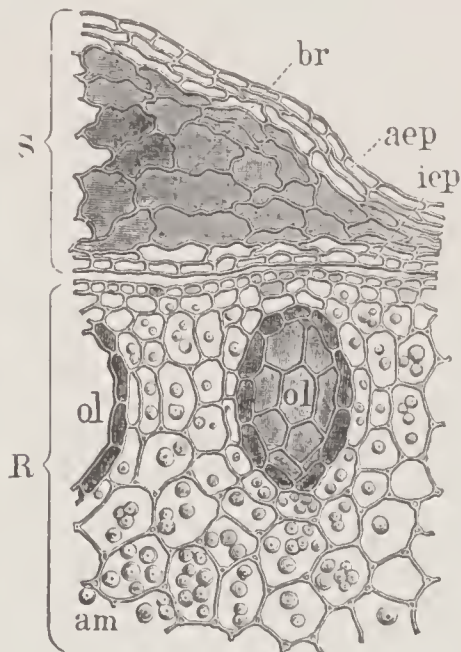


FIG. 104.

FIG. 104.—Allspice. Seed in cross section. *S* spermoderm: *aep* outer epidermis; *br* brown cells; *iep* inner epidermis. *R* radicle: *ol* volatile oil cavities; *am* starch grains. $\times 160$. (A.L.W.)

hol and treatment with sodium hydroxide is advisable. The consolidated tissues may be grouped as (1) *epicarp* (*epi*) of small cells, stomata, and short thickwalled, often crooked, hairs (*t*); (2) *volatile oil zone*, the cavities (*ol*) reaching or exceeding 200 μ in radial diameter; (3) *mesocarp* of ground parenchyma with fibro-vascular bundles (*fv*) running through the middle portion, and various types of colorless stone cells (*st*) distributed throughout the tissues; (4) *compressed parenchyma* (*c*); and (5) *endocarp* also of the compressed cells.

Oxalate crystals (*cr*) occur in many of the parenchyma cells, especially between and immediately within the volatile oil cavities. Simple crystals (Fig. 105, *cr*) occur in the partition.

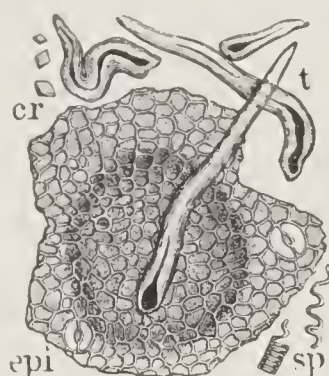


FIG. 105.

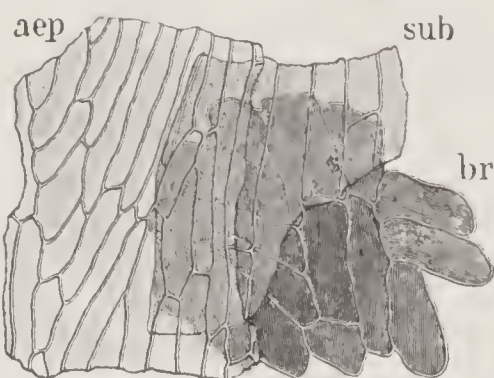


FIG. 106.

FIG. 105.—Allspice. Pericarp in surface view: *epi* epicarp with *t* hair and two stomata, over volatile oil cavity; *sp* spiral vessels of mesocarp; *cr* crystals of partition wall. $\times 160$. (A.L.W.)

FIG. 106.—Allspice. Spermoderm in surface view: *aep* outer epiderm; *sub* sub-epiderm; *br* brown cells. $\times 160$. (A.L.W.)

The *stone cells* occur singly or in groups. Their form, size, and wall thickening vary greatly.

In the partition the ground tissues are mostly compressed, volatile oil cavities are lacking, and stone cells are relatively few.

Spermoderm (Fig. 104, S; Fig. 106).—Four layers are differentiated: (1) *outer epiderm* (*aep*) of longitudinally elongated, colorless cells, sometimes with a tendency to herringbone arrangement; (2) *sub-epidermal cells* (*sub*) forming a single or double layer of elongated cells broader than those of the outer epiderm; (3) *brown parenchyma* (*br*), thickest on the outer convex and inner flat sides, of variously elongated cells containing material of a clear rich red-brown color; and (4) *inner epiderm* (*iep*) similar to the outer epiderm.

English authors, beginning with Hassall, refer to the *brown parenchyma* as port wine cells. The contents stain blue or green with ferric chloride.

Perisperm and Endosperm.—Only traces present.

Embryo.—The radicle (Fig. 104, *R*) has an *epiderm* of small starch-free cells, a zone with *volatile oil cavities* (*ol*) as in the pericarp, and *ground parenchyma* containing round or truncated starch grains (*am*) up to 12 μ , with distinct hilum, often in small aggregates.

CHIEF STRUCTURAL CHARACTERS.—Fruit rough, brown, globular, 8 mm., two-celled and two-seeded, with four minute calyx lobes. Seed deep brown; embryo spiral with large radicle and minute cotyledons.

Epicarp with stomata and short, thick-walled hairs; mesocarp with volatile oil cavities, fibro-vascular bundles, and numerous colorless stone cells. Spermoderm with conspicuous brown (port wine) cells; radicle with volatile oil cavities as in mesocarp and ground tissue containing starch. Starch grains up to 12 μ , round or truncated, with distinct hilum, occurring singly or in small aggregates.

CHEMICAL COMPOSITION.—Allspice being a spice of minor importance, the literature is meager. The analyses which follow are by Richardson¹ and Winton, Ogden, and Mitchell²:

COMPOSITION OF ALLSPICE

	Water	Protein	Oil, fixed	Oil, volatile*	Starch, pure†	Starch, Crude ‡	Fiber	Crude tannin§	Ash, total	Ash, soluble	Sand
	%	%	%	%	%	%	%	%	%	%	%
Richardson.....	6.19	4.38	6.15	5.15	14.83	10.97	4.01
W. O. and M.:											
Min.....	9.45	5.19	4.35	3.38	1.82	16.56	20.46	8.06	4.15	2.29	0.00
Max.....	10.14	6.37	7.72	5.21	3.76	20.65	23.98	12.48	4.76	2.69	0.06
Aver. (3).....	9.78	5.75	5.84	4.05	3.04	18.03	22.39	9.71	4.47	2.47	0.03

* Volatile ether extract. † Diastase method. ‡ Reducing matter, after washing with 10% alcohol and direct inversion of residue, calculated as starch. § Tannin equivalent to oxygen absorbed.

Winton, Ogden, and Mitchell found 7.39 to 14.27, average **11.79**, per cent of alcohol extract in allspice.

The *U. S. Standards* require that allspice contain not less than 8 per cent of quercitannic acid (calculated from the total oxygen ab-

¹ U. S. Dept. Agr., Div. Chem. 1887, Bul. **13**, 11, 227.

² Connecticut Agr. Exp. Sta. Rep. 1898, p. 184.

sorbed by the aqueous extract) and not more than 25 per cent of fiber, 6 per cent of total ash, nor 0.4 per cent of sand.

Volatile Oil.—Oil of pimento or oil of allspice closely resembles oil of cloves, but has a lower eugenol content, hence ground clove stems substituted for the ground product would escape detection if only the eugenol content were considered. By the Von Fellenberg chromic acid oxidation method, Zäch¹ obtained 3 to 5 per cent of volatile oil.

Physical and Chemical Values.—The limits tabulated below are compiled from the standards of the British, German, and American Pharmacopœias, as well as from other sources. The hydrogen numbers are by Albright.²

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot. 25° C.	Hydrogen No.	Eugenol	Sol. 70% alcohol
			°		%	vols.
Min.	1.024	1.525	−4	97.8	65	1
Max.	1.055	1.537	0	97.8	90	2

English and German authorities give the minimum specific gravity at 15° C. as 1.030 and 1.024 respectively.

Two analyses of pimento leaf oil by Chiris³ show: specific gravity at 15° C. 1.0407 and 1.0342, saponification number 9.8 and 11.2, and eugenol 70 and 69 per cent. Kemp⁴ found the specific gravity of a single sample to be 1.062 at 19° C.

Constituents.—The chief constituent of allspice oil was shown by Oeser⁵ to be identical with the *eugenol* of cloves. Its properties, as well as those of other constituents, are described under Cloves and Cassia. Other constituents given by Schimmel & Co.⁶ are *caryophyllene*, *methyl eugenol*, *cineol*, *l-α-phellandrene*, and *palmitic acid*.

Kemp⁷ isolated from pimento leaf oil a solid acid (C₁₃H₁₄O₄), melting at 78° C., and a liquid acid (C₁₀H₁₄O₄), boiling under a pressure of 1.7 mm. at 70 to 73°.

¹ Mitt. Lebensm. Hyg. 1932, **23**, 156.

² J. Am. Chem. Soc. 1914, **36**, 2188.

³ Parf. France 1924, **15**, 107.

⁴ Arch. Pharm. 1925, **263**, 12.

⁵ Ann. 1864, **131**, 277.

⁶ Rep. Apr. 1904, 75.

⁷ Loc. cit.

Bay or Myreia oil from the leaves of *P. acris* Kostel, according to Power and Klerber,¹ contains eugenol, methyl eugenol, chavicol, methyl chavicol, citral, *l*-phellandrene, and myrcene.

Tannin.—See Cloves.

Pentosans.—In dry matter 11.29 per cent. See also Introduction to Part III.

¹ Pharm. Runds. 1885, **13**, 60.

FRUITS OF THE PARSLEY FAMILY

(*Umbelliferæ*)

IN the introduction to Roots of the Parsley Family, Volume II, are listed umbelliferous food plants including fruits (commonly known as "seeds"), grouped according to tribes.

While umbelliferous roots and leaves are valuable for their nutrients, the minute amount of volatile oil being incidental, fruits of the family are produced primarily for the volatile oil, to which each fruit owes its characteristic flavor and for which alone it is used in human foods. Only in the case of the residues from the distillation of the volatile oils, which are fed to cattle, is the nutritive value of the fruit taken into consideration.

The fruit is used either as such in bread, cake, confectionery, pickles, condiments, and meat dishes or in the form of volatile oil, obtained by distillation, in confectionery, cordials, drugs, etc.

COMPARATIVE MACROSCOPIC STRUCTURE.—The ovary of the flower with its two cells, each containing an ovule, develops on fertilization into the *fruit* with its two carpels known as *mesocarps*. Not only do the fruits, often with part of their pedicels, separate from the umbel on threshing, but the mericarps tend to separate from each other on the commissure and hang suspended from the top of the stemlike *carpophore*.

The *carpophore* of coriander is entire, that of celery forks near the top, of caraway near the center, of anise about one-third the distance from base to top, of cumin near the base, and of fennel and dill at the very base.

Five primary *ribs*, each with a *fibro-vascular bundle*, run longitudinally from base to apex of each mericarp. Secondary ribs occur in coriander and cumin. Under a lens anise is hairy, cumin bristly, the remaining fruits smooth. Dill has broad wings, instead of ribs, at the commissure.

Normally a single *vitta* or *oil duct* is present in the mesocarp beneath each channel separating the ribs, and two are in the mesocarp on the commissural side. In anise, however, several and in cumin one to three *vittæ* occur beneath each channel, while in coriander the whole

middle tissue of the mesocarp on the dorsal side is replaced by a hard, fibrous tissue to the complete exclusion of vittæ.

The *seed* is anatropous. On the dorsal side the spermoderm is reduced to a thin skin; on the commissural side it broadens into a soft tissue surrounding the raphe. The bulky *endosperm* forms the greater part of the seed, and the small *embryo*, varying from one-quarter to one-half the length of the fruit, is embedded in the upper part of the endosperm.

COMPARATIVE MICROSCOPIC STRUCTURE.—In the second edition of Moeller's *Mikroskopie der Nahrungs- und Genussmittel* and the two editions of Winton's *Microscopy of Vegetable Foods* is given an analytical key to umbelliferous fruits, prepared by one of us. This key, although sufficient for identifying the members of the group in powder form, does not give certain additional distinguishing characters which are included in the following table.

	Epicarp	Mesocarp sclerenchyma	Vittæ beneath each channel	Endocarp cells	
				Breadth	Arrangement
Coriander	crystals	fibers	none	narrow*	transverse†
Cumin	bristly	none	1	broad‡	“
Dill	smooth	reticulated cells, fibers§	1	narrow*	parqueted
Fennel	“	reticulated cells	1	“	“
Anise	hairy	none	5–10	broad‡	transverse†
Caraway	striated	“	1	“	“
Celery	papillose	reticulated cells	1–3	narrow*	“

* Usually less than 7 μ . † Usually more than 7 μ . ‡ Except on commissure. § In wings.

CHIEF STRUCTURAL CHARACTERS.—Pericarp with vittæ containing volatile oil. Seed with bulky endosperm in which the small embryo is embedded.

Mesocarp sclerenchymatous, endocarp of elongated cells variously arranged, endosperm containing aleurone grains and fatty oil. Styger and Zörnig¹ classify 50 umbelliferous fruits according to their histological structure.

COMPARATIVE CHEMICAL COMPOSITION.—The volatile oils contain the following characteristic constituents; minor constituents

¹ Schweiz. Apoth. Ztg. 1919, 57, 3, 17, 29, 48, 67, 84, 94, 105, 125, 143, 170, 183, 199, 214, 228, 243.

are given under each spice: *coriander*, coriandrol the chief constituent; *cumin*, cuminal the characteristic but not the chief constituent; *dill*, carvone the chief constituent; *fennel*, anethole the chief, fenchone the characteristic, constituent; *anise*, anethole the chief constituent, methyl chavicol and anisaketone present; *caraway*, carvone and limonene present in approximately equal amounts; *celery*, limonene the chief, sedanolide the characteristic, constituent; *parsley*, apiole the chief constituent.

CORIANDER

Coriandrum sativum L.

Fr. Coriandre. Sp. Cilantro. It. Corianderlo. Ger. Koriander.

Although probably a native of northern Africa and the Near East, coriander is grown throughout the temperate zone.

The fruit differs materially in form, structure, and the nature of its volatile oil from the other common species of the family. It is much used in confectionery and in the manufacture of cordials.

MACROSCOPIC STRUCTURE (Fig. 107).—The nearly globular fruit (I, II) crushes readily because of the hollow space between the mericarps. The *carpophore* is entire, that is, not forked. Under a lens the five main ribs of each mericarp appear wavy on the surface; the six secondary ribs, straight. Since the marginal secondary ribs of the two mericarps (IV) are in such close contact as to form a single double rib at each edge, the total number of secondary ribs for the whole fruit is ten. *Vittæ* are present only on the commissural side. On the dorsal side the inconspicuous fibro-vascular bundles are outside the dense fiber zone forming the middle tissues of the pericarp.

MICROSCOPIC STRUCTURE (Fig. 108). **Pericarp**.—Excepting the endocarp, the tissues are quite different from those of the other members of the group: (1) *epicarp* (*epi*) of polygonal cells with indistinctly knotty walls, each containing a single crystal or crystal group of calcium oxalate; (2) *outer mesocarp* of large, polygonal cells passing into elongated cells about the fibro-vascular bundles located in the inner part; (3) *fiber layer* (*f*) with thick-walled elements more or less bent, crossing in different layers; (4) *inner mesocarp* (*mes*) of large, polygonal cells with somewhat thickened and, adjoining the endocarp, also beaded walls; and (5) *endocarp* (*end*) of long, very narrow cells, occasionally parqueted.

The *fibro-vascular bundles* are small and contain narrow pitted (*pi*) and spiral (*sp*) vessels. On the commissural side where the fiber

layer is lacking the polygonal cells encasing the vittæ (*v*) have beaded walls.

Spermoderm.—The *outer epiderm* (*aep*) of polygonal cells contains formless yellowish brown contents.

Endosperm.—The *aleurone cells* (*al*) have thick walls, and the aleurone grains reach $12\ \mu$ with a beautiful oxalate crystal in the larger ones.

Embryo.—Small, thin-walled cells.



FIG. 107.

FIG. 108.

FIG. 107.—Coriander. I side view. $\times 1$. II side view. $\times 3$. III longitudinal section of single mericarp. $\times 3$. IV cross section: pericarp (white) with fiber layer (dark gray) and commissural vittæ (oval); spermoderm, narrow broadening on commissure; endosperm (light gray); cotyledons (oval). $\times 8$. (A.L.W.)

FIG. 108.—Coriander. Elements of fruit in surface view. *epi* epicarp; *f* fiber layer; *pi* pitted vessels; *sp* spiral vessel; *mes* inner mesocarp; *v* vitta; *end* endocarp. *aep* outer epiderm of spermoderm. *al* aleurone cells of endosperm. $\times 160$. (A.L.W.)

CHIEF STRUCTURAL CHARACTERS.—Fruit globular with ten wavy primary and ten straight secondary ribs. Carpophore entire. Vittæ only on commissural side.

Epicarp cells with oxalate crystals; mesocarp on exposed sides with dense fiber layer; mesocarp cells encasing vittæ beaded; inner mesocarp of polygonal, thickened or beaded cells; endocarp of very narrow cross cells.

CHEMICAL COMPOSITION.—Analyses of the whole fruit by Arnst and Hart¹ and a summary of 8 analyses of the dried distillation resi-

¹ Z. angew. Chem. 1893, 6, 136.

due by Uhlitzsch ¹ are given below. With regard to the starch found by Arnst and Hart, see Anise.

COMPOSITION OF WHOLE CORIANDER AND DISTILLATION RESIDUE

	Water	Protein	Protein, pure	Oil, fixed	Oil, volatile	N-f. ext.	Sugar	Starch	Fiber	Ash	Sand
	%	%	%	%	%	%	%	%	%	%	%
Fruit....	11.31	12.03	19.17	0.23	25.75	1.92	10.53	26.23	5.28
Residue:											
Min....	5.50	11.25	13.00*	16.20	23.80	15.00	5.70	1.40†
Max....	9.66	16.60	14.80*	20.20	32.80	26.50	12.70	4.40†
Aver...	7.58	14.29	13.63*	17.68	29.18	22.45	8.81	1.49†

* 3 analyses. † 4 analyses.

The *U. S. Standards* limit total ash to 7 per cent and acid-insoluble ash to 1.5 per cent.

Fixed Oil.—*Physical and Chemical Values* by Grimme,² Rakuzin and Starobina,³ Norkin,⁴ and Vanin and Chernoyarova⁵ have the following range:

	Sp. gr. 15° C.	Ref. ind. 25° C.	Solid. point	Sapon. No.	Iodine No.	Acid No.	Fatty acids, titer	Unsa- ponifi- able matter
			°C.				°C.	%
Min...	0.9110	1.4692	−2	182.0	72.8	1.3	1	0.73
Max...	0.9284	1.4722	−4	204.9	99.8*	7.8	1	2.26

* Wijs.

Volatile Oil.—Zäch,⁶ by Von Fellenberg's chromic acid oxidation method, obtained 0.3 to 1.5 per cent. Sankevich ⁷ found that the whole fruit contains 0.42 per cent of volatile oil of which 44.3 per cent is in the hull (pericarp).

¹ Landw. Vers.-Stat. 1893, **42**, 215.
² Pharm. Zentralh. 1911, **52**, 661.
³ Landw. Vers.-Stat. 1924, **103**, 103.
⁴ Masloboino Zhirovoe Delo 1929, No. 8, 25.
⁵ J. Appl. Chem. (U.S.S.R.) 1933, **6**, 922.
⁶ Mitt. Lebensm. Hyg. 1932, **23**, 156.
⁷ Masloboino Zhirovoe Delo 1936, **12**, 389.

Physical and Chemical Values.—German, English, and American authors give substantially the same limits for specific gravity, optical rotation, and alcohol solubility. In the table which appears below, the limits for *d*-linaloöl are those reported by Schimmel & Co.¹ and are higher than those of the British Pharmaceutical Codex (45 to 65 per cent); those for total alcohols and ester number after formylation on which they are based represent 9 normal samples analyzed by Chiris.²

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Ester No.	Formyl No.*	Acid No.	<i>d</i> -Lin- aloöl	Total alco- hols	Sol. 70% al- cohol
			°				%	%	vols.
Min...	0.870	1.460	+ 8	20	214	0.2	60	65	2
Max...	0.888	1.471	+14	20	253	5.0	70	79	3

* Ester number after formylation.

The results on Calabrian oil by LaFace,³ on Indian oil by Rao, Sudborough, and Watson,⁴ on Rumanian oil by Kopp,⁵ and on Hungarian oils by Janicsek⁶ conform in general to the above limits.

The oil from the green leaves, as determined by Kopp,⁵ shows specific gravity at 15° C. 0.872, refractive index at 20° C. 1.4574, optical rotation 0.9°, ester number 35.5, acid number 17.0, and linaloöl 81.7 per cent, also insoluble in 70 per cent alcohol up to 20 volumes.

Spiridonova⁷ determined the yield and physical values of the oil distilled from the various parts of the plant during five stages from flowering to full maturity of seed. The specific gravity increases from 0.83 to 0.86, and the optical rotation, which is only 0 to 1.73 during flowering, increases with the increase in *d*-linaloöl.

Constituents.—About two-thirds of coriander oil consists of the alcohol *coriandrol* (*d*-linaloöl). The following minor constituents are given by Walbaum and Müller⁸: the terpenes *d*- and *dl*- α -pinene, β -pinene, phellandrene (?), cymene, dipentene, α -terpinene, γ -ter-

¹ Rep. 1909, 47.

² Parf. France 1924, 21, 320.

³ Ibid. 1924, 21, 326.

⁴ J. Indian Inst. Sci. 1925, 8A, 143.

⁵ Pharm. Zentralh. 1929, 70, 789.

⁶ Mezőgazdasági Kutatások 1929, 2, 153.

⁷ J. Gen. Chem. (U.S.S.R.) 1936, 6, 1536.

⁸ Wallach Festschrift 1909, 654.

pinene, and *terpinolene* (?); the alcohols *geraniol* and *l-borneol*; the acetic esters of these and *d-linaloöl*, and *n-decylic aldehyde*.

Prepared at the flowering stage, coriander volatile oil yielded in an investigation by Karlblom¹ 10 per cent of *n-decylaldehyde* and two decylene isomers, namely *2-decen-1-aldehyde* and *8-methyl-2-nonen-1-aldehyde*. By oxidation, decylic, octylic, and oxalic acids were obtained.

Coriandrol or *d-linaloöl*, $C_{10}H_{18}O$ or $(CH_3)_2C : CH \cdot CH_2 \cdot CH_2 \cdot C(CH_3)OH \cdot CH : CH_2$, an alcohol discovered by Kawalier² and named by Semmler,³ occurs in coriander oil; the levo-form is more widely distributed, being found in oils of various citrus fruits, thyme, sassafras, etc. It is a fragrant liquid; specific gravity at 15° C. 0.867, boiling point 197 to 199° C., and optical rotation +20° *circa*. By oxidation, it passes into its inactive isomer *geraniol*.

Pentosans.—In dry matter 11.77 per cent. See also Introduction to Part III.

CUMIN

Cuminum Cyminum L.

Fr. Cumin. Sp. Comino. It. Comino di Malta. Ger. Kreuzkümmel.

Since ancient times cumin fruits have been prized as a flavoring in Egypt, Palestine, and adjacent regions where the plant is native. Although of secondary importance as a spice, the plant is grown on a commercial scale in the Mediterranean region and in kitchen gardens of both hemispheres.

Cumin is used to flavor certain types of Dutch cheese, in medicine, for cordials, and in cooking.

MACROSCOPIC STRUCTURE (Fig. 109).—The *fruit* (I) varies in length up to 7 mm. It is indistinctly beaked. In addition to the five primary ribs, which are smooth under a lens, there are four secondary ribs over the *vittæ* with distinct bristles (III). Harz, however, shows bristles on all the ribs and Hager only on the primary ribs. The *carphore* is forked near the base, and the embryo is about half the length of the fruit (II). In cross section (IV) the fruit is crescent-shaped.

MICROSCOPIC STRUCTURE.—Two characters distinguish cumin from fennel and caraway, which it otherwise resembles: (1) the *emer-*

¹ Bul. Appl. Bot., Genetics Plant Breeding (U.S.S.R.), 1936, Ser. III, No. 13, 53.

² Ann. 1852, 84, 351.

³ Ber. 1891, 24, 206.

gences (bristles) which on the primary ribs are short (Fig. 110, I, II) and on the secondary ribs are elongated (III), and (2) the transversely elongated cells of the *endocarp* which on the central commissural side toward the apex are sclerenchymatized, abruptly passing into short, irregularly extended cells (Fig. 111).

The *epicarp* (Fig. 110) is more or less striate. Compared with the corresponding layer of caraway, the cross cells of the *endocarp* are narrower, and longitudinal elongation on the commissural side is not the rule.

CHIEF STRUCTURAL CHARACTERS.—Secondary ribs with long bristles. Carpophore forked near base.

Epicarp with emergences, long over secondary ribs, short over primary ribs; endocarp cells mostly broad although narrower than in caraway, transversely elongated (not parqueted as in fennel), sclerenchymatized on commissural side toward apex, passing into irregularly elongated forms.

CHEMICAL COMPOSITION.—König¹ gives the only proximate analysis of the whole fruit found in the literature which, together with 2 analyses of the dried distillation residue by Uhlitzsch,² follow:

COMPOSITION OF WHOLE CUMIN AND DISTILLATION RESIDUE

	Water	Protein	Oil, fixed	Oil, volatile	N-f. ext.	Sugar	Starch *	Pento- sanes	Fiber	Ash	Sand
	%	%	%	%	%	%	%	%	%	%	%
Fruit	19.34	17.88	12.87	2.19	3.76	6.01	7.09	6.52	7.80
Residue:											
Damascus.	6.00	16.40	20.80	32.90	9.80	14.10	1.60
Aleppo. . . .	5.60	14.30	13.40	34.50	10.90	21.30†	4.40

* See note under Anise.

† CaCO₃, 7.16%.

The *U. S. Standards* limit total ash to 9.5 per cent, acid-insoluble ash to 1.5 per cent, and harmless foreign matter to 5 per cent.

¹ Chem. mensh. Nahr.-Genussm., Berlin, 1920, 2, 849.

² Landw. Vers.-Stat. 1893, 42, 215.



FIG. 109.—Cumin. I side view. $\times 1$. II side view, mericarps separated. $\times 2$. III dorsal view. $\times 2$. IV cross section: pericarp (white) with bundles (black) and vittae (oval); spermoderm, narrow, broadened at commissure; endosperm (gray); cotyledons (oval). $\times 8$. (A.L.W.)

Fixed Oil.—*Physical and Chemical Values* of the oil obtained by extraction by Grimme¹ follow: yield 9.9 per cent, specific gravity at 15° C. 0.9256, refractive index at 25° C. 1.4756, solidifying point −8° C., saponification number 179.3, iodine number 91.8, ester number 176, acid number 3.3, and unsaponifiable matter 2.06 per cent.

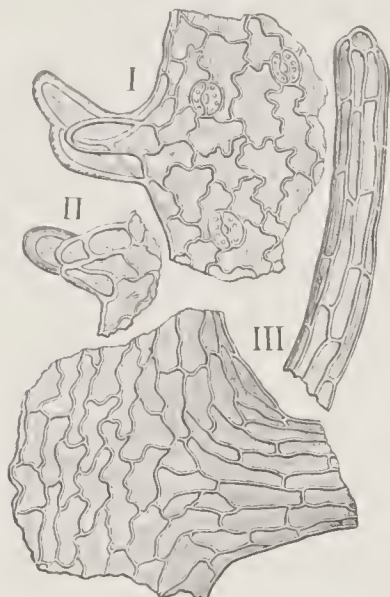


FIG. 110.

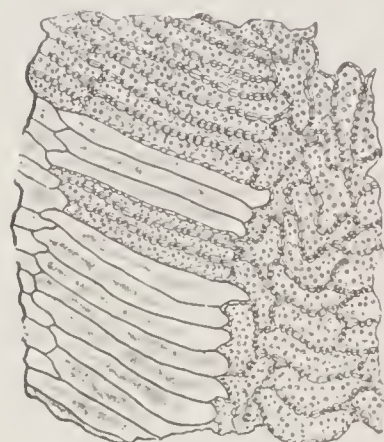


FIG. 111.

FIG. 110.—Cumin. I, II epicarp with small emergences from primary rib. III epicarp with long emergence from secondary rib. $\times 160$. (A.L.W.)

FIG. 111.—Cumin. Endocarp from central commissural side near apex showing thin-walled and sclerenchymatized cells. $\times 160$. (A.L.W.)

Volatile Oil.—The content of volatile oil varies from 2 to 4 per cent.

Physical and Chemical Values.—The oil from Levantine fruit is heavier and less soluble in 80 per cent alcohol than that from East Indian fruit, which explains the wide range in values as given herewith:

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Aldehydes	Sol. 80% alcohol
			°	%	vols.
Min.....	0.890	1.491	+3	16	3
Max.....	0.930	1.507	+8	18	11

Persian oil, examined by Umney,² showed: specific gravity at 15° C. 0.911, refractive index 1.4980, optical rotation +7°, and aldehydes 18 per cent.

¹ Pharm. Zentralh. 1911, 52, 661.

² Perf. Ess. Oil Rec. 1913, 4, 43.

Indian oil obtained by steam distillation of white cumin, as examined by Rao, Sudborough, and Watson,¹ showed: yield 2.35 per cent, specific gravity at 15° C. 0.8945, refractive index at 25° C. 1.4910, optical rotation at 25° C. 3.6°, soluble in 11 volumes of 80 per cent alcohol at 20° C., and aldehydes 16 per cent.

Constituents.—*Cuminal*, first identified by Bertagnini,² is the characteristic constituent but makes up hardly a fifth of the oil. In addition the terpene *cymene*, as shown by Warren,³ and another terpene, “*hydrocuminene*,” are present. Berenguer⁴ found a trace of *cuminic acid*.

Cuminal or cumin aldehyde, $C_{10}H_{12}O$ or $(CH_3)_2CH \cdot C_6H_4 \cdot CHO$, is a heavy liquid, specific gravity at 15° C. 0.972, boiling point 237° C., which by treatment with alcoholic potassium hydroxide splits up into cuminic alcohol and cuminic acid. It is prepared by precipitation from cumin oil with sodium bisulphite and decomposition of the cuminal sodium bisulphite with sodium carbonate.

Hydrocuminene, $C_{10}H_{16}$, specific gravity at 15° C. 0.860, boiling point 157° C. (768 mm.), was described by the Russian chemist Wolpian, but has not been thoroughly studied.

DILL

Anethum graveolens L.

Fr. Aneth. Sp. Eneldo. It. Aneto. Ger. Dille.

In various regions about or east of the Mediterranean and Caspian Seas dill is said to grow wild. Its cultivation is widespread, the fruits being used in medicine and for flavoring condiments. Dill pickles, originally prepared by German housewives, are now packed on a commercial scale in the United States. In these it is a common practice to use not only the fruits but whole heads with part of the stalk.

MACROSCOPIC STRUCTURE (Fig. 112).—From other fruits of the group dill is distinguished by the broad *wings* at the edge of the commissure, replacing the lateral ribs of the other species. A cross section (IV) shows that the *fibro-vascular bundles* in these wings are large. The dorsal ribs and *vittæ* are the same in numbers and arrangement as in fennel and caraway. The *carpophore* is divided.

¹ J. Indian Inst. Sci. 1925, 8A, 143.

² Ann. 1853, 85, 275.

³ Jahrb. Chem. 1865, 514.

⁴ Anal. soc. españ. fis. quim. 1933, 31, 189.

MICROSCOPIC STRUCTURE (Fig. 113).—Radial longitudinal sections through the wings show (1) *epicarp* (*epi*); (2) *hypoderm* of one or two rows of isodiametric, beaded cells; (3) *palisade cells* (*pal*), forming two rows; (4) *fibers* (*f*); (5) *fibro-vascular bundles* with spi-



FIG. 112.

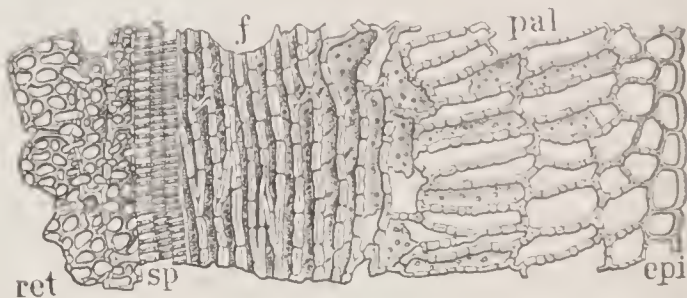


FIG. 113.

FIG. 112.—Dill. I dorsal view. $\times 1$. II dorsal and III ventral view. $\times 2$. IV cross section showing wings. $\times 8$. (A.L.W.)

FIG. 113.—Dill. Longitudinal radial section through wing. *epi* epicarp; *pal* palisade cells; *f* fibers; *sp* spiral vessels; *ret* reticulated vessels and cells. $\times 160$. (A.L.W.)

ral (*sp*) and reticulated vessels; (6) *reticulated cells* (*ret*); and (7) *mesocarp* ground tissue (not shown).

Layers 2 to 6 inclusive are of sclerenchymatized cells; the remainder of the fruit and seed is not sufficiently different from that of fennel to warrant description.

CHIEF STRUCTURAL CHARACTERS.—Fruit winged. Carpophore divided.

Wings with two rows of palisade cells and numerous sclerenchyma fibers.

CHEMICAL COMPOSITION.—The *U. S. Standards* limit total ash to 10 per cent and sand to 3 per cent.

A summary of 3 analyses of the dried residue from the distillation of the volatile oil by Uhlitzsch ¹ follows:

COMPOSITION OF THE DISTILLATION RESIDUE

	Water	Protein	Oil, fixed	N-f. ext.	Fiber	Ash
	%	%	%	%	%	%
Min.....	7.4	14.5	15.5	34.7	14.7	8.5
Max.....	8.0	15.6	18.0	36.1	16.4	9.8
Aver.....	7.8	15.1	16.8	35.5	15.8	9.0

¹ Landw. Vers.-Stat. 1893, 42, 215.

Fixed Oil.—*Physical and Chemical Values* by Grimme ¹ and Rakuzin and Starobina ² are here summarized:

	Sp. gr. 15° C.	Ref. ind. 26° C.	Solid. point	Sapon. No.	Iodine No.	Acid No.	Fatty acids, titer	Unsapon- fiable matter
			° C.				°C.	%
Min.....	0.9282	−2	176.0	91.5	3.1	1	1.14
Max.....	0.9291	1.4831	−2	188.7	119.6*	3.1	2	1.14

* Wijs.

Volatile Oil.—The oil yield varies from 2 to 4 per cent.

Physical and Chemical Values.—English and German dill oils vary within the following limits, as shown by analyses given by Umney,³ Parry,⁴ Gildemeister and Hoffmann,⁵ and others:

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Carvone	Sol. 80% alcohol
			°	%	vols.
Min.....	0.895	1.480	+70	40	4
Max.....	0.924	1.495	+88	60	9

Spanish dill yielded abnormal oil with specific gravity at 15° C. 0.903 and optical rotation +50.3°.

Japanese oil differs from European, Umney's analyses showing specific gravity at 15° C. 0.9643 and optical rotation +50°.

Indian oil, the product of *A. sowa* Roxb., resembles the Japanese. Umney found specific gravity at 15° C. 0.9486, optical rotation +47°; Rao, Sudborough, and Watson⁶ found specific gravity at 15° C. 0.9785, refractive index at 25° C. 1.4943, optical rotation at 25° +47.6°. Rao et al. also examined separately the light and heavy oils respectively with the following results: yield 2.17, 1.02 per cent; specific gravity at 15° C. 0.9313, 1.0935; refractive index at 25° C. 1.4853, 1.5154; optical rotation at 25° C. (light) +58°.

¹ Pharm. Zentralh. 1911, **52**, 661.

² Landw. Vers.-Stat. 1924, **103**, 103.

³ Pharm. J. 1898, [4], **7**, 176.

⁴ Allen: Com'l. Org. Anal., Philadelphia, 1917, **9**, 340.

⁵ Ätherischen Öle, Leipzig, 1931, **3**, 527.

⁶ J. Indian Inst. Sci. 1925, **8A**, 143.

Oil of the dill plant (not fruit) grown in Spain, as examined by Fritzsche Brothers,¹ had a lower specific gravity (0.9062 at 15° C.) and higher refractive index (1.4119 at 20° C.) than that from European fruit.

Constituents.—*Carvone*, as found by Gladstone,² is the chief constituent, the amount present being usually somewhat less than in caraway oil (which see). Wallach³ isolated *d-limonene*, and Schimmel & Co.⁴ demonstrated the presence of *phellandrene*. Another terpene ($C_{10}H_{16}$) appears to be present.

According to Ciamician and Silber,⁵ Indian oil contains *dill-apiole*, $C_{12}H_{14}O_4$ or $C_6H(CH_2 \cdot CH : CH_2)(O_2 : CH_2)(O \cdot CH_3)_2$, an isomer of the apiole of parsley.

Dill plant oil has been found by Schimmel & Co.⁶ to contain *myristicin* and *isomyristicin*.

Guenther⁷ states that by distilling dill seeds and dill plants yields of 2.35 to 3.5 and 0.29 to 1.5 per cent of oil respectively are obtained. Both contain *carvone*, *phellandrene*, and *d-limonene*. In exceptional cases, the seed oil contains over 60 per cent of *carvone*. *Terpinene*, *dillapiol*, *isomyristicin*, and *myristicin* are minor constituents.

FENNEL

Fœniculum vulgare Mill. = *F. officinale* All.

Fr. Fenouil. Sp. Hinojo. It. Finocchio. Ger. Fenchel.

Fennel grows wild throughout the Mediterranean region eastward to Persia and is grown in gardens throughout Europe and America.

Among the countries supplying the market with fennel are Germany, Greece, Italy, Crete, Persia, India, and Japan. The fruit of Florence fennel is shipped from southern France in considerable quantities.

Dry fennel fruit, as a "seed" for bread, cakes, and confectionery, ranks with caraway, anise, and coriander. The volatile oil is used in drugs and cordials. The needle-shaped leaves of both the type and

¹ Schimmel & Co. Rep. Nov. 1908, 49.

² Jahresb. Chem. 1872, 25, 1.

³ Ann. 1885, 227, 292.

⁴ Rep. Apr. 1897, 15.

⁵ Ber. 1896, 29, 1799.

⁶ Rep. 1927, 36.

⁷ Am. Perf. 1938, 36, No. 6, 48.

Florence fennel (which see) are used to some extent in salads and various dishes.

MACROSCOPIC STRUCTURE (Fig. 114). *Fruit* of common fennel (I, II) from cultivated plants in extreme cases reaches 10 mm. in length but usually is less than 8 mm. while that from wild plants is smaller still. Florence fennel has larger fruits reaching 12 mm.

The two *mericarps* (III) are slightly bowed at the commissure and are suspended from tips of the divided *carpophore*. Each mericarp has five *ribs*, which are least prominent in fruits of wild plants, and each rib contains a fibro-vascular bundle. A comparison of Fig. 114,

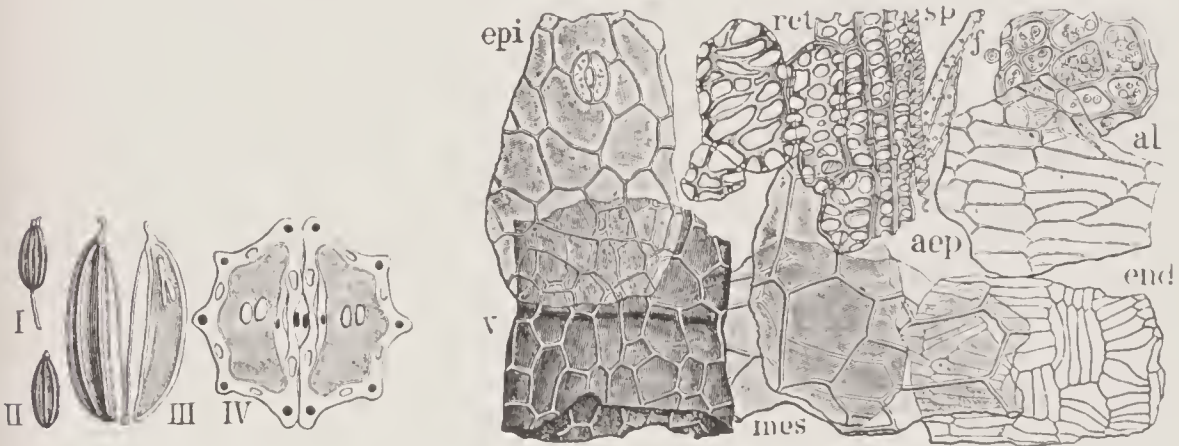


FIG. 114.

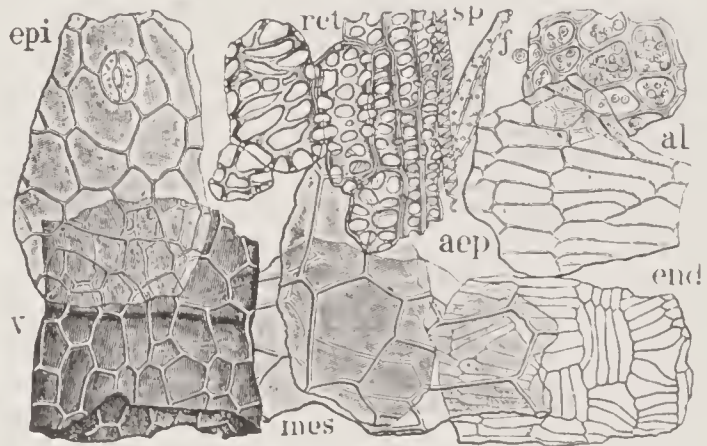


FIG. 115.

FIG. 114.—Fennel. I side and II dorsal view of whole fruit. $\times 1$. III mericarps suspended from carpophore. $\times 3$. IV cross section: pericarp (white) with bundles (black) and vittæ (oval); spermoderm, narrow, expanded at commissure; endosperm (gray); cotyledons (oval). $\times 8$. (A.L.W.)

FIG. 115.—Fennel. Elements of fruit in surface view. Pericarp: *epi* epicarp; *mes* mesocarp ground tissue; *v* vitta; *sp* spiral vessel; *ret* reticulated vessels passing into reticulated parenchyma; *f* bast fibers; *end* endocarp. Spermoderm: *aep* outer epiderm. Endosperm: *al* aleurone cells. $\times 160$. (A.L.W.)

IV with Fig. 118, III shows that the cross section of fennel, examined under a lens, is narrower than that of caraway, that the angles formed at the commissure are acute, not obtuse as in caraway, and that the vittæ are narrower although in both there is one beneath each channel and two on the commissural side of each mericarp. At the center of the commissural side the spermoderm, which elsewhere is thin, is broadened to contain the raphe. The embryo (Fig. 114, III, right, above) is about one-third the length of the bulky endosperm, the radicle and cotyledons being of about equal length.

MICROSCOPIC STRUCTURE (Fig. 115). **Pericarp.**—The tissues are (1) *epicarp* (*epi*) of smooth, non-porous polygonal cells and occa-

sional stomata; (2) *mesocarp* (*mes*) of isodiametric or longitudinally elongated cells in the outer and transversely elongated cells in the inner layers, through which run vittæ (*v*) and fibro-vascular bundles; and (3) *endocarp* (*end*) of very narrow parqueted cells.

The cells incasing the vittæ are polygonal-isodiametric, smaller than those of the remainder of the mesophyl parenchyma. Flanking each fibro-vascular bundle are *reticulated cells* (*ret*), passing into reticulated vessels which, together with *spiral vessels* (*sp*), constitute the xylem. *Bast fibers* (*f*) also accompany the fibro-vascular bundles.

Spermoderm.—Only the *outer epiderm* (*aep*) of transversely elongated cells shows definite structure at maturity.

Endosperm.—The cells (*al*) are rather thick-walled and contain aleurone grains up to 10 μ and fat. Each large aleurone grain usually incloses a rosette of calcium oxalate.

Embryo.—Small thick-walled cells.

CHIEF STRUCTURAL CHARACTERS.—Fruit smooth, thinner than caraway, usually acute-angled at commissure. Carpophore divided. Vittæ one beneath each channel but narrower than in caraway.

Epicarp not striated or beaded; reticulated cells adjoin fibro-vascular bundles; endocarp cells very narrow, parqueted.

CHEMICAL COMPOSITION.—A single analysis of the fruit by Arnst and Hart¹ and a summary of 9 analyses of the dried distillation residue by Uhlitzsch² are tabulated below. The presence of starch reported by Arnst and Hart may be due to the use of a method that converts constituents other than starch into copper reducing matter or to the presence of starchy impurities. True starch is present in small amount, if at all, in the fruit.

COMPOSITION OF WHOLE FENNEL AND DISTILLATION RESIDUE

	Water	Protein	Protein, pure	Oil, fixed	Oil, volatile	N-f. ext.	Sugar	Starch	Fiber	Ash	Sand
	%	%	%	%	%	%	%	%	%	%	%
Fruit.....	17.19	16.28	8.86	2.89	32.44	4.71	14.33	13.74	8.60
Residue:											
Min....	5.40	13.80	12.70*	12.00	20.24	12.50	7.20	0.50†
Max....	11.60	21.50	12.70*	18.50	38.70	25.95	13.40	1.30†
Aver...	8.30	16.76	12.70*	15.17	31.12	18.28	10.37	0.97†

* 1 analysis. † 3 analyses.

¹ Z. Angew. Chem. 1893, 6, 136.

² Landw. Vers.-Stat. 1893, 42, 215.

The *U. S. Standards* limit total ash to 9 per cent and sand to 2 per cent.

Fixed Oil. *Physical and Chemical Values.*—Results by Grimme¹ and Rakuzin and Starobina² range as follows:

	Sp. gr. 15° C.	Ref. ind. 20° C.	Sapon. No.	Iodine No.	Acid No.
Min.....	0.930	178	98	...
Max.....	0.931	1.4831	183	99	3.1

Volatile Oil.—By the Von Fellenberg chromic acid method, Zäch³ obtained 2 to 6 per cent.

Physical Values as compiled from various sources are given below. The hydrogen number is by Albright.⁴

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Solid. point	Hydrogen No.	Sol. 80% alcohol
			°	°C.		vols.
Min.....	0.946	1.525	+ 5	+ 3	101.3	5
Max.....	0.980	1.541	+24	+12	102.7	8

Results by Umney⁵ for Roman or sweet fennel oil, Macedonian oil, Indian oil (*F. panmorium* DC.); and Japanese oil, by LaFace⁶ for Roman oil, and by Rao, Sudborough, and Watson⁷ for Indian fennel oil fall within the above limits. Rutovskii and Tzyurikh⁸ and Sobyenin and Saakov,⁹ in their examination of Russian oil from the Poltawa and Krasnodar districts respectively, obtained results warranting the minimum specific gravity and maximum refractive index given in the above table. Guenther¹⁰ reports results on Moroccan oils quite different from those given above, as follows: specific gravity at

¹ Pharm. Zentralh. 1911, 52, 661.

² Landw. Vers.-Stat. 1924, 103, 103.

³ Mitt. Lebensm. Hyg. 1932, 23, 156.

⁴ J. Am. Chem. Soc. 1914, 36, 2188.

⁵ Pharm. J. 1896, 3, 91, 216; 1897, 4, 225.

⁶ Parf. France 1924, 21, 326.

⁷ J. Indian Inst. Sci. 1925, 8A, 143.

⁸ Trans. Sci. Chem. Pharm. Inst. Moscow 1924, 10, 69; Chem. Abs. 1926, 20, 3773.

⁹ Masloboino Zhirovov Delo 1929, No. 6, 34.

¹⁰ Drug Cosm. Ind. 1938, 42, 439.

20° C. 0.879, refractive index at 20° C. 1.4689, and optical rotation +57.5°.

According to Wallach,¹ bitter fennel oil from plants grown in France, Spain, and Algiers has low specific gravity (0.905 to 0.925) and high rotation (+48°) due to high *d*-phellandrene content and low anethole content. Sicilian oil from *F. piperitum* is low in specific gravity (0.951) and anethole content and has a rotation of -5°.

Rom² determined the silver iodide number, which he states ranged from 100 to 120 for normal oil with an anethole content of 63.6 to 76.8 per cent, not 50 to 60 per cent as usually given.

Constituents.—*Anethole*, constituting over half, and the ketone *fenchone*, about 20 per cent, are the chief constituents of the oil. Other substances that are present (although not in all samples) are the terpenes *d*-pinene, *dipentene*, *limonene*, *α*-phellandrene, and possibly *cymene*. *Aniseketone* and *methyl chavicol* were identified by Tardy.³

The constitution and properties of anethole, aniseketone, and methyl chavicol are described under Anise.

Fenchone, C₁₀H₁₆O or C₆H₇O(CH₃):C(CH₃)₂, discovered by Wallach and Hartmann,⁴ is a ketone similar to camphor, which it resembles in odor. There are two modifications, one dextro- the other levorotatory. The former, a characteristic constituent of volatile fennel oil, is a liquid; specific gravity at 15° C. 0.948; optical rotation +71.7°; boiling point 192 to 194° C.; melting point after solidifying by cooling +5° C.

Sage and Goodale⁵ state that Spanish oil contains little fenchone.

Pentosans.—In dry matter 5.90 per cent. See also Introduction to Part III.

ANISE

Pimpinella Anisum L.

Fr. Anis. Sp. Anís. It. Anice. Ger. Anis.

From the eastern Mediterranean, probably the original home of the plant, the culture of anise has been extended to most parts of Europe and thence over the world. Spanish, French, Italian, German, and Russian anise enter into commerce. The best product is used as

¹ Ann. 1887, **238**, 78.

² Pharm. Monatsh. 1934, **15**, 287.

³ Bul. soc. chim. 1897, III, **17**, 660.

⁴ Ann. 1891, **263**, 129.

⁵ Perf. Ess. Oil Rec. 1922, **13**, 18.

such for cakes, condiments, and meat dishes, inferior grades being utilized for the manufacture of the volatile oil for which there is a large demand by manufacturers of confectionery, cordials, and medicinal preparations. In this connection it should be stated that commercial oil of anise is in large part obtained from star anise, the fruit of another family, the two products, although reacting somewhat differently to qualitative tests, being hardly distinguishable in flavor and general properties.

MACROSCOPIC STRUCTURE (Fig. 116).—In two marked respects anise fruit differs from all the other members of the group here described: (1) it is hairy, the hairs being visible under a good lens;

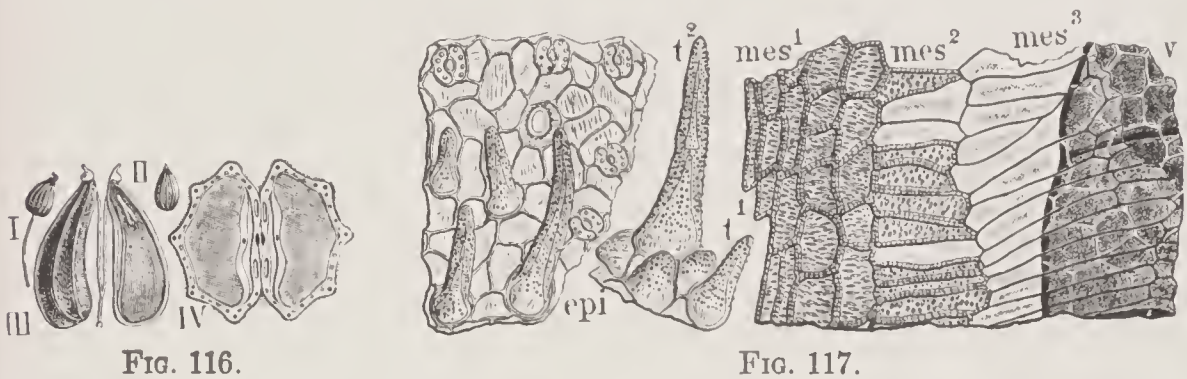


FIG. 116.

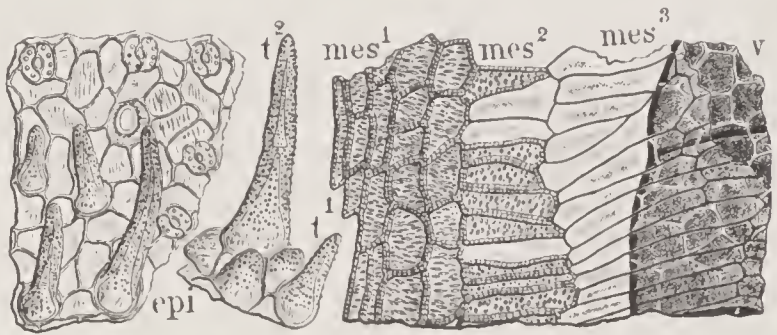


FIG. 117.

FIG. 116.—Anise. I side and II dorsal view of whole fruit. $\times 1$. III mericarps suspended from carpophore. $\times 4$. IV cross section: pericarp (white) with bundles (black) and vittæ (oval); spermoderm thin, broadened at commissure; endosperm (gray). $\times 8$. (A.L.W.)

FIG. 117.—Anise. Elements of pericarp in surface view. *e*_{pi} epicarp with *t*¹ unicellular and *t*² dicellular hairs; *v* vitta; *mes*¹, *mes*² sclerenchyma cells and *mes*³ thin-walled cells of endocarp from commissure near apex. $\times 160$. (A.L.W.)

and (2) it has usually over twenty-five and often forty or more vittæ in each mericarp.

In some varieties the ovoid, whole fruit (I, II) reaches 6 mm. in length, but in others seldom exceeds 4 mm. In longitudinal section (III) the embryo is one-quarter as long as the fruit. The *carpophore* is entire for about one-third of its length. In cross section (IV) two large vittæ are seen on the commissural side of each mericarp, the remainder being on the exposed surface.

MICROSCOPIC STRUCTURE (Fig. 117).—Characteristic of the numerous hairs are their blunt, conical form and thick, strongly warty walls. Usually they are unicellular (*t*¹), but some of the large hairs are dicellular (*t*²). Because of the warts, when seen head on they appear to be surrounded by a string of beads (*e*_{pi}, above center).

The *endocarp* on the exposed part of the pericarp consists of long cross cells (*e*), rarely parqueted, broader and longer than those of fennel, but not so broad as those of caraway. On the commissural side toward the apex they abruptly become isodiametric or longitudinally elongated and sclerenchymatized (*mes*¹).

The *vittæ* (*v*), being numerous on the exposed sides, are necessarily much narrower than those on the commissural side.

Except for the above characters the fruit and seed tissues are not distinctive.

CHIEF STRUCTURAL CHARACTERS.—Fruit ovoid, hairy with numerous vittæ. Carpophore entire one-third its length.

Hairs warty, thick-walled, one- to two-celled. Endocarp cross cells intermediate in width between those of fennel and caraway, rarely parqueted, abruptly isodiametric or longitudinally elongated and sclerenchymatized at commissure.

CHEMICAL COMPOSITION.—Analysis of 2 varieties of whole anise by Arnst and Hart¹ and a summary of 11 analyses by Uhlitzsch² of the dried residue from the distillation of the volatile oil, excluding one showing 27.9 per cent of sand, are given below. The percentage of starch reported by Arnst and Hart may be due to the use of a method that converts constituents other than starch into copper reducing matter or to the presence of starchy impurities. True starch is present in small amount, if at all, in the fruit.

COMPOSITION OF WHOLE ANISE AND DISTILLATION RESIDUE

	Water	Pro- tein	Pro- tein, pure	Oil, fixed	Oil, vola- tile	N-f. ext.	Sugar	Starch	Fiber	Ash	Sand
	%	%	%	%	%	%	%	%	%	%	%
Fruit											
A. and H.:											
Russia....	12.75	18.09	9.95	0.78	35.91	5.50	5.40	12.10	10.42
Levant....	12.81	18.15	10.45	1.01	37.00	3.42	4.86	14.59	5.99
Residue											
Uhlitzsch:											
Min.....	4.84	16.40	14.80*	16.40	16.11	8.70	9.07	0.80†
Max.....	8.84	18.90	17.30*	27.00	36.00	28.36	16.90	8.60†
Aver.....	6.91	18.00	16.07*	19.79	28.59	14.36	12.35	4.57†

* 3 samples. † 7 samples.

The *U. S. Standards* limit total ash to 9 per cent and sand to 1.5 per cent.

¹ Z. angew. Chem. 1893, 6, 136.

² Landw. Vers.-Stat. 1893, 42, 215.

Fixed Oil. *Physical and Chemical Values.*—Limits based on analyses by Demjanow and Zyplenkow,¹ Grimme,² and Rakuzin and Starobina³ follow:

	Sp. gr. 15° C.	Ref. ind.	Solid. point	Sapon. No.	Iodine No.	Acid No.	Fatty acids, titer
			°C.			%	°C.
Min.....	0.9232	1.4710	−3	178.4	102.9	1.9	0.0
Max.....	0.9302	1.4738	−3	187.1	108.6	6.3	0.0

Volatile Oil.—The volatile oil of anise and star anise are much alike in properties. The yield from anise is from 2 to 3 per cent. Zäch,⁴ by Von Fellenberg's chromic acid oxidation method, obtained 2 to 6 per cent.

Physical and Chemical Values.—The limits for physical constants in the following table are consistent with those of the U. S. Pharmacopœia; those for hydrogen number are by Albright.⁵

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Solid. point	Boiling point	Hydrogen No.	Anethole	Sol. 90% alcohol
			°	°C.	°C.		%	vols.
Min.....	0.975	1.544	−2	+14	232	125.8	80	1.5
Max.....	0.993	1.556	+1	+19	234	127.3	90	3.0

The *U. S. Standards* require 3 per cent by volume of anise oil in anise extract.

Crimean oil, examined by Rutovskii and Leonov,⁶ shows a polarization of +12.2°.

Constituents.—*Anethole* is the chief constituent. *Methyl chavicol*, reported by Schimmel & Co.,⁷ and *aniseketone*, first found by Bouchardet and Tardy,⁸ are minor constituents of both anise and star anise oils.

¹ J. Russ. Phys.-Chem. Ges. 1905, **36**, 621.

² Pharm. Zentralh. 1911, **52**, 661.

³ Landw. Vers.-Stat. 1924, **103**, 103.

⁴ Mitt. Lebensm. Hyg. 1932, **23**, 156.

⁵ J. Am. Chem. Soc. 1914, **36**, 2188.

⁶ Trav. Sci. Chim. Pharm. Inst. Moscou 1924, No. 10, 64; Chem. Abs. 1928, **22**, 2437.

⁷ Rep. Oct. 1895, 7.

⁸ Compt. rend. 1896, **122**, 198.

In Crimean oil, Rutovskii and Leonov found *phellandrene* but no fenchone; in Russian oil they ¹ found *α-phellandrene*, *d-fenchone*, *d-α-pinene*, *dipentene*, *camphene*, and *anisealdehyde*.

Anethole or para-methoxypropylbenzene, $C_{10}H_{12}O$ or $C_6H_4(CH : CH \cdot CH_3)(OCH_3)$ (see Introduction to Part III), is the chief constituent of anise and star anise oil and also occurs in fennel oil. It crystallizes as plates from anise oil on cooling and may be further purified by crystallization from alcohol. It is also obtained by heating with alcoholic potassium hydroxide, methyl chavicol, an isomer, and by heating methoxyphenylcrotonic acid. Since its melting point is about 22° C., it is commonly considered to be a liquid. Its specific gravity at 25° C. is 0.986; its boiling point is about 234° C. Albright ² reports a hydrogen number of 150.5. In alcohol and ether, anethole is readily soluble, in water only slightly.

Methyl chavicol, $C_{10}H_{12}O$ or $C_6H_4(OCH_3)(CH_2 \cdot CH : CH_2)$, is the chief constituent of tarragon oil; it occurs also in anise, star anise, bay, and basil oils. It is a liquid with a faint anise odor; boiling point 215° C.; specific gravity at 15° C. 0.972. The substance has been synthesized by Verley ³ and Tiffeneau.⁴

Aniseketone or methoxybenzylmethylketone, $C_6H_4(OCH_3 \cdot CO \cdot CH_3)(CH_2)$. Tardy ⁵ discovered this substance in Russian anise oil. Chiris ⁶ found in star anise oil about 1 per cent of aniseketone with the following values: specific gravity at 15° C. 1.086; boiling point at 760 mm. pressure 263°; melting point of oxime 72° C.

Pentosans.—In dry matter 5.64 per cent. See also Introduction to Part III.

CARAWAY

Carum Carvi L.

Fr. Carvi. Sp. Alcaravea. It. Carvi. Ger. Kümmel.

As a native plant caraway occurs in many regions of Europe and western Asia and as a cultivated plant chiefly in Russia, Holland, Scandinavia, and parts of Germany. It is grown sparingly in the United States and has run wild in some regions.

¹ Trans. Sci. Chem. Pharm. Inst. Moscou 1928, No. 4, 16; Chem. Abs. 1929, **23**, 239.

² J. Am. Chem. Soc. 1914, **36**, 2188.

³ German patent.

⁴ Compt. rend. 1904, **138**, 985.

⁵ Thesis, Paris, 1902.

⁶ Parf. France 1926, **38**, 119.

The dried fruits are much used in bread and cookies, and the volatile oil is the characteristic flavoring of Kümmel.

MACROSCOPIC STRUCTURE (Fig. 118).—Both fennel and caraway have thread-shaped leaves. The *carpophore* forks at about the middle. The *fruit* (I, II) is shorter than fennel; in cross section (III) each mericarp is nearly regularly pentagonal, the angles at the carpophore being obtuse, approaching right angles. The number and location of the *vittæ* are the same as in fennel.

MICROSCOPIC STRUCTURE (Fig. 119).—Only the tissues noticeably different from those of fennel are described. The *epicarp* (*epi*), unlike that of fennel, when mature is longitudinally striated and the walls are beaded. *Reticulated cells* do not as in fennel accompany the



FIG. 118.

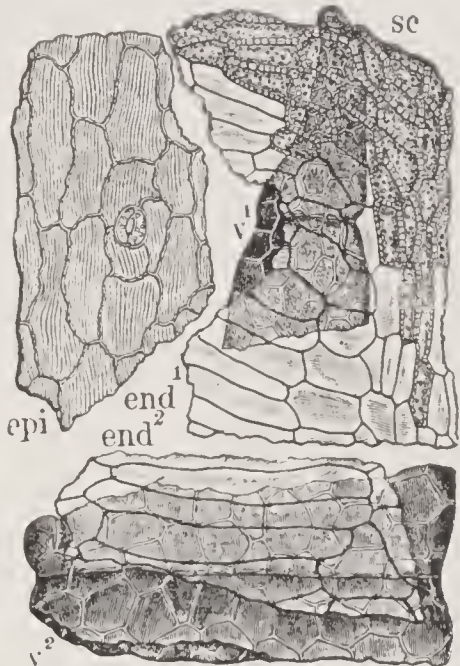


FIG. 119.

FIG. 118.—Caraway. I single mericarp. $\times 1$. II mericarps suspended from carpophore. $\times 2$. III cross section: pericarp (white) with bundles (black) and vittæ (oval); spermoderm, narrow, expanded at commissure; endosperm (gray); cotyledons (oval). $\times 8$. (A.L.W.)

FIG. 119.—Caraway. Elements of pericarp in surface view. *epi* epicarp; v^1 vitta at apex, v^2 at base; end^1 endocarp at apex, end^2 at base; *sc* sclerenchyma cells of endocarp. $\times 160$. (A.L.W.)

fibro-vascular bundles. The most striking distinction from fennel is the much broader cross cells of the *endocarp* (end^1 , end^2), which are not parquered, although on the central commissural side they abruptly pass into longitudinally elongated cells. Another striking characteristic, common to both transversely and longitudinally elongated cells, is the abrupt transition of thin-walled into beaded sclerenchyma cells at the apex of the mericarp.

CHIEF STRUCTURAL CHARACTERS.—Fruit smooth, thicker than fennel, usually obtuse-angled at commissure. Carpophore forked in middle. Vittæ, one in each channel but broader than in fennel.

Epicarp striated and beaded; reticulated cells adjoining fibro-vascular bundles absent; endocarp cells broad, not parqueted, but sclerenchymatized at apex and longitudinally elongated on central commissural side.

CHEMICAL COMPOSITION.—An analysis by Arnst and Hart,¹ included in the table below, shows 4.53 per cent of starch which may be due to starchy impurities or the use of a faulty method. True starch is not present in appreciable amount in umbelliferous fruits. The percentage of fixed oil is low. An analysis of the dried distillation residue by Dyer and Gilbard² and a summary of 14 analyses by Uhlitzsch³ are also given.

COMPOSITION OF WHOLE CARAWAY AND DISTILLATION RESIDUE

	Water	Protein	Protein, pure	Oil, fixed	Oil, volatile	N-f. ext.	Fiber	Ash, total	Ash, soluble	Sand
	%	%	%	%	%	%	%	%	%	%
Fruit										
A. and H.:	15.87	20.25	8.81	3.78	27.10*	17.73	6.46
D. and G.:										
I.....	12.30	20.40	1.90	6.10	2.10	0.30
II.....	11.20	19.50	1.50	6.70	2.20	0.40
Residue										
D. and G.:	6.90	16.10	0.10	6.70	2.20	0.40
Uhlitzsch:										
Min....	6.10	18.31	19.70†	13.40	17.27	12.60	6.10	0.20‡
Max....	12.00	23.90	21.80†	20.16	36.10	27.04	10.30	1.00‡
Aver...	8.90	21.45	20.75†	16.53	29.39	16.34	7.39	0.60‡

* Includes sugar 4.10 and starch equivalent 4.53%. † 2 samples. ‡ 3 samples.

The *U. S. Standards* require that caraway seed contain not more than 8 per cent of total ash nor more than 1.5 per cent of sand.

Fixed Oil.—The *Physical and Chemical Values* by Grimme⁴ and Rakuzin and Starobina⁵ are summarized below:

¹ Z. angew. Chem. 1893, 6, 136.
² Analyst 1896, 21, 207.
³ Landw. Vers.-Stat. 1893, 42, 215.
⁴ Pharm. Zentralh. 1911, 52, 661.
⁵ Landw. Vers.-Stat. 1924, 103, 103.

	Sp. gr. 15° C.	Ref. ind. 25° C.	Sapon. No.	Iodine No.
Min.....	0.9213	1.4746	178.3	104.8
Max.....	0.9268	1.4746	183.6	128.5

Volatile Oil.—The yield of volatile oil is variously stated from 3 to 7 per cent, indicating that the percentages given in the table above are low. Crops grown in the vicinity of Haarlem, Holland, contained, according to Zijlstra,¹ 3.75 to 5.32 per cent of volatile oil. Zäch,² by Von Fellenberg's chromic acid oxidation method, obtained 2 to 5 per cent.

Physical and Chemical Values.—The following limits are based on available data:

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot. 25° C.	Sol. 80% alcohol	Carvone
			°	vol.	%
Min.....	0.907	1.484	70	2	45
Max.....	0.920	1.498	85	10	65

Values of caraway oil produced in Rumania from cultivated Dutch, cultivated Rumanian, and wild seed, examined by Kopp,³ and of Russian oil distilled from pure seed, examined by Pigulevskii and Nikitina,⁴ fall within the above limits. In Hungarian oil Janicsek⁵ found 50.19 and Guenther⁶ 55.8 per cent of carvone. Oil distilled from mixtures of Russian seed and pulp had a higher specific gravity (0.946 at 15° C.) and lower optical rotation ($\alpha_D +65^\circ$). Oil from chaff of Tunisian seed examined by Chiris⁷ was high in specific gravity (0.9325 at 15° C.) and low in rotation ($+46^\circ$) but normal in refractive index (1.4878 at 20° C.).

¹ Monograph: Med. Hoog. Land. Tuin Boschbouwsw. 8.

² Mitt. Lebensm. Hyg. 1932, **23**, 156.

³ Pharm. Zentralh. 1927, **68**, 212.

⁴ J. Russ. Phys. Chem. Soc. 1920, **51**, 72.

⁵ Kísérletügyi Közlemények 1934, **37**, 147.

⁶ Am. Perf. 1938, **36**, No. 3, 48.

⁷ Parf. France 1924, **16**, 152.

Constituents.—Wallach¹ estimated that 50 to 60 per cent of normal caraway oil consists of *d-carvone*, the carvol of Gladstone,² and nearly all the remainder of *d-limonene*. Kopp³ found 56 to 62 and Zijlstra⁴ 47 to 54 per cent. Schimmel & Co.⁵ reports small amounts of *dihydrocarvone*, $C_{10}H_{16}O$ or $C_6H_8(OH_3)(O)(C_3H_5)$ (specific gravity at 15° C. 0.9297, optical rotation -16.3° , boiling point 221° C. at 735 mm., melting point of oxime 89° C., of dibromide 70° C.), *dihydrocarveol*, $C_{10}H_{18}O$ or $C_6H_9(CH_3)(OH)(C_3H_5)$ (specific gravity 0.9368, optical rotation -6.23° , boiling point 101° C. at 7 to 8 mm.), and an unknown base with a narcotic odor. Blumann and Zeitschel⁶ identified *carveol*, $C_{10}H_{15}O_2$, as a constituent.

Carvone or carvol, $C_{10}H_{14}O$ or $C_6H_6(CH_3)(O)(C_3H_5)$, is a liquid ketone to which Tiemann and Semmler assign the above formula (see structural formula under Introduction of Spices). According to this formula, carvone has only one double bond in the ring, whereas its isomers thymol and carvacrol have three. The substance has *d*-, *l*-, and inactive forms, the *d*-form occurring in caraway and dill oils, the *l*-form in spearmint oil. Wallach⁷ has synthesized carvone from terpineol and transformed carvone again into terpineol. The physical values of *d*-carvone are: specific gravity at 15° C. 0.964, optical rotation $+62^\circ$, and boiling point 224° C. (230° C., Schimmel & Co.).

Pentosans.—In dry matter, caraway 6.86, Roman caraway 7.82 per cent. See also Introduction to Part III.

CELERY

Apium graveolens L.

Fr. Céleri. Sp. Apio. It. Appio. Ger. Sellerie.

Valuable for its seeds as well as its petioles (Volume II) and roots, this species among umbelliferous plants is comparable with *Brassica oleracea* among crucifers. The variety furnishing edible roots is known as celeriac (which see). Celery seed is produced on a commercial scale in France. It is used for seasoning and is an ingredient of certain mixtures, one of which is known as celery salt.

¹ Ann. 1893, **275**, 110.

² J. Chem. Soc. 1872, **25**, 1.

³ Loc. cit.

⁴ Loc. cit.

⁵ Rep. Apr. 1905, 19.

⁶ Ber. 1914, **47**, 2623.

⁷ Papers in Ann. 1888 et seq.

MACROSCOPIC STRUCTURE (Fig. 120).—Whole celery *fruits* (I) are distinguished from all other members of the group by their small size (up to 1.6 mm.) and spherical form. A longitudinal section (II) shows the mericarps suspended on a carpophore forked near the top. In cross section (III) the shape is like that of caraway, but is distinguished by the smaller size and frequent presence of two or three vittæ in each channel.

MICROSCOPIC STRUCTURE (Fig. 121).—The *epicarp* (*epi*) is striated like that of caraway, but the walls are not beaded, the outer wall often being developed into papillæ. As in fennel, *reticulated cells* (*ret*) accompany the fibro-vascular bundles, especially near the



FIG. 120.

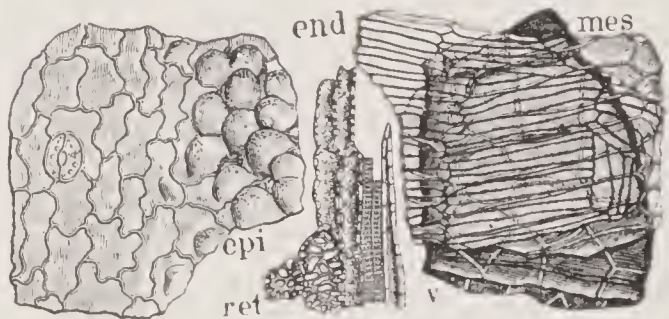


FIG. 121.

FIG. 120.—Celery. I whole fruit. $\times 1$. II mericarps suspended from carpophore. $\times 5$. III cross section: pericarp (white) with bundles (black) and vittæ (oval); spermoderm, narrow, broadened at commissure; endosperm (gray). $\times 8$. (A.L.W.)

FIG. 121.—Celery. Elements of pericarp in surface view. *epi* epicarp; *mes* mesocarp ground tissue; *ret* reticulated cells accompanying bundle; *v* vitta; *end* endocarp. $\times 160$. (A.L.W.)

apex of the fruit. The cross cells of the *endocarp* (*end*), although occasionally parqueted as in fennel, as a rule are characterized only by their narrow breadth and great elongation.

CHIEF STRUCTURAL CHARACTERS.—Fruit small, spherical. Carpophore forked near top. Each mericarp nearly equilateral pentagonal. Vittæ often two to three in each channel.

Epicarp striated as in caraway, often papillose; reticulated cells similar to those of fennel accompany fibro-vascular bundles; endocarp of narrow, mostly much-elongated cross cells, occasionally parqueted as in fennel.

CHEMICAL COMPOSITION.—The *U. S. Standards* limit total ash to 10 per cent and sand to 2 per cent. They further require that

celery seed extract contain not less than 0.3 per cent by volume of celery seed oil.

Fixed Oil.—Grimme¹ by ether extraction secured 16.7 per cent of a green-brown oil from celery seed with the following values: specific gravity at 15° C. 0.9236, refractive index at 25° C. (recalculated) 1.4819, solidifying point −12°, saponification number 178.1, iodine number (Wijs) 94.8, ester number 176.3, acid number 1.8, solidification point of fatty acids −4° C., and unsaponifiable matter 0.79 per cent.

Volatile Oil.—The yield of oil by steam distillation varies from 2 to 3 per cent. The range based on results given by Schimmel & Co.,² Swenholt,³ and Gildemeister and Hoffmann⁴ follows:

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Ester No.	Acetyl No.*	Acid No.	Sol. 90% alcohol
			°				vols.
Min.....	0.860	1.478	+ 51	16	43	0	6
Max.....	0.898	1.486	+100	55	67	4	8

* Ester number after acetylation.

More recent results by Chiris⁵ follow: specific gravity at 15° C. 0.9165, optical rotation +55° 45', ester number 74.9, and acid number 1.12.

The light fraction of a sample by Swenholt³ showed: specific gravity at 20° C. 0.8408, optical rotation +111.7°, and had a limonene odor; the heavy fraction showed: specific gravity at 20° C. 0.8774, optical rotation +75°, and had a celery odor.

Constituents.—Results obtained in the laboratory of Schimmel & Co.⁶ indicate that *d*-limonene is the chief constituent and that pinene is absent. The characteristic flavor appears to be due to the oxygenated compounds *sedanolide* (C₁₂H₁₈O₂) and *sedanonic acid anhydride* (C₁₂H₁₆O₂) discovered by Ciamician and Silber,⁷ who also isolated *palmitic acid*, a *guaiacol-like phenol*, a *phenol* (C₁₆H₂₀O₃) melting at 66 to 67° C., a *sesquiterpene*, and a mixture of *terpenes*.

¹ Pharm. Zentralh. 1911, **52**, 661.

² Schimmel & Co. Ber. Apr. 1902.

³ Midl. Drug. 1910, **44**, 220.

⁴ Ätherischen Öle, Leipzig, 3 Aufl. 1931, **3**, 471.

⁵ Parf. France 1936, **14**, 12.

⁶ Rep. Apr. 1892, 15; Apr. 1910, 32.

⁷ Ber. 1897, **30**, 492, 501, 1419, 1424, 1427.

Schimmel & Co.¹ further investigated the sesquiterpene and named it *selinene*. Ruzicka and Stoll² separated from the high-boiling fraction a sesquiterpene alcohol, C₁₅H₂₆O.

Schimmel & Co. give the following proportions of constituents: limonene 60, *d*-selinene 10, various alcohols 2.5 to 3, sedanolide 2.5 to 3, and sedanonic acid anhydride 0.5 per cent.

Sedanolide has been assigned the constitutional formula C₆H₈(CH·C₄H₉)O(CO). It is a lactone boiling at 185° C. under 17 mm. pressure.

Sedanonic acid anhydride, C₆H₈(C:C₄H₈)O(CO), is sedanonic acid (C₁₂H₁₈O₃), a ketonic acid, less H₂O.

PARSLEY

Petroselinum sativum Hoffm. = *Apium Petroselinum* L.

Fr. Persil. Sp. Perejil. It. Prezzemolo. Ger. Petersilie.

The fruit itself is not used as a spice, but the oil prepared therefrom is of interest because of its relation to the oil present in the leaves and stems (see Vegetables, Volume II).

MACROSCOPIC AND MICROSCOPIC STRUCTURE.—See Harz.³

CHEMICAL COMPOSITION. Fixed Oil.—The fruit contains about 20 per cent of fixed oil.

Volatile Oil.—Oil is distilled from the fruits, herb, and root, the yield from the fruits varying up to 6 per cent and from the leaves and root each up to 0.1 per cent.

Physical and Chemical Values.—The following limits represent extreme results:

	Sp. gr. 15° C.	Ref. ind. 20° C.	Opt. rot.	Ester No.	Acetyl No. *	Acid No.	Sol. 80% alcohol
			°				vols.
Min.....	1.043	1.480	−10	1	4	0	4
Max.....	1.100	1.528	−4	11	20	6	8

* Ester number after acetylation.

¹ Rep. Apr. 1910, 96.

² Helv. Chim. Acta 1923, 6, 852.

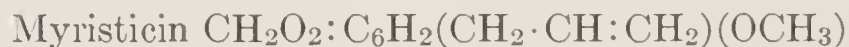
³ Samenkunde, Berlin, 1885, p. 1039.

Constituents.—*Apiole*, $C_{12}H_{14}O_4$, is the chief constituent. Its structural formula was first derived by Thoms,¹ who also identified other constituents of the oil. Bignami and Testoni² isolated a substance shown by Thoms to be *myristicin*. In French oil Thoms also found *palmitic acid* and unidentified *phenols*, *aldehydes*, and *ketones*.

Chavalier³ states that French oil differs from German oil in containing very little apiole but a considerable amount of myristicin. Matthes and Heintz,⁴ in material furnished by Vongerichten and Köhler,⁵ obtained, by crystallization from ether, leaflets melting at 69° C. of *petrosilane* ($C_{20}H_{42}$), corresponding to the bryonane of Etard⁶ and the laurane of Matthes and Sander,⁷ also resembling the hydrocarbon isolated by Schwalb⁸ from beeswax.

Apiole, or parsley camphor, crystallizes in needles melting at 30° C. and boiling at about 294° C. On boiling with alcoholic potassium hydroxide, it is converted into isapiole which has somewhat higher melting and boiling points.

The structural formulas of the three related substances, according to Thoms, are as follows:



“*Apiols*” are viscous commercial preparations, specific gravity 1.05 to 1.09, consisting chiefly of apiole. They are classified by color. Lutz and Oudin⁹ give tests for purity, also viscosity coefficients as follows: green 9 to 13, yellow 7 to 10, white 5.5 to 6.5.

¹ Ber. 1903, **36**, 1714, 3446, 3452; 1908, **41**, 2753.

² Gaz. chim. ital. 1900, **30**, I, 240.

³ Bul. gén. therap. 1910, **158**, 101.

⁴ Ber. pharm. Ges. 1909, **19**, 325.

⁵ Ber. 1909, **42**, 1638.

⁶ Compt. rend. 1892, **114**, 365.

⁷ Arch. Pharm. 1908, **246**, 173.

⁸ Dis., Tübingen, 1884.

⁹ Ann. fals. 1920, **3**, 335, 395.

FRUITS OF THE NIGHTSHADE FAMILY

(*Solanaceæ*)

SEE also chapter on Solanaceous Fruits in Volume II. Vegetables, Legumes, and Fruits.

PAPRIKA

Capsicum annuum L.

Fr. Piment des jardins. Sp. Pimiento. It. Peperone. Ger. Paprika.

Paprika is the Hungarian name for the large, mildly pungent fruits of a variety of *C. annuum* L. grown in Hungary and surrounding regions. The powdered spice is used in various native dishes, notably *Gulasch* and *Paprikahuhn*. During recent years the fame of powdered paprika has spread from the Continent to the United States where fruits of other varieties, grown in other regions such as Spain, Mexico, Louisiana, and South Carolina, are substituted for true paprika. In Spain the name *pimiento* designates the product of that country and in Mexico other names are current, but in English-speaking countries paprika has come to include various kinds of mild red pepper ground as a spice. Some of the varieties described under the head of *Capsicums* are used for the purpose, but usually they are so hot that the ground product is substituted for cayenne.

As there are garden varieties of peppers varying from "mild" or "sweet" to "hot," so also the ground spice varies in pungency according to its source.

Hungarian and Spanish paprika are stated to be indistinguishable in appearance.

Four grades of the ground spice are prepared in Hungary: (1) Sweet paprika (free from seeds, stems, and placentæ); (2) Rosenpaprika (free from stems but not placentæ—in the best grade free from seeds); (3) Königspaprika (often includes stems and placentæ); and (4) low grades prepared by grinding waste from preceding products. The value of paprika depends on its delicate flavor, being inversely proportional to its pungency.

In addition to the dried pods and ground spice, canned peppers (pimentos), free from seeds, for use in salads, are an important article of commerce.

MACROSCOPIC STRUCTURE.—The *peduncle* (fruit stem) is hollow, up to 5 mm. in diameter, broadening to the coarse flattened calyx which has five to six obtuse lobes. A part of the peduncle and all the calyx are commonly attached to the dried fruit of commerce.

Characteristic of the *pericarp* (Fig. 122) are its blunt conical form, up to 12 cm. long, smooth, lustrous surface, and deep red, almost black



FIG. 122.—Commercial varieties of red peppers. Top row: Hungarian Paprika, Bombay Capsicum, South Carolina Capsicum. Bottom row: Bombay Cherry Capsicum, Zanzibar Cayenne, Naples Chilli. $\times \frac{1}{2}$. (A.L.W.)

color. It is two- or three-celled at the base, with the same number of central placentæ, but unicellular toward the apex with parietal placentæ. The dissepiments (partition walls) forming the cavities secrete minute drops which with a lens are often seen on the surface or held in cavities beneath the cuticle. These contain capsaicin, the highly pungent principle. Although numerous, the seeds do not fill the cavity, hence the dried pod is more or less flattened.

The campylotropous *seed* is flattened, up to 5 mm. in diameter. The spermoderm is leathery, the endosperm bulky. Embedded in the latter is the coiled embryo with cotyledons longer than the radicle. The microphyle adjoins the hilum in a slight projection on the edge of the seed.

MICROSCOPIC STRUCTURE. Peduncle.—No sharp boundary exists between peduncle (fruit stem) and calyx. At some distance from the calyx the woody peduncle consists of (1) *epiderm* of rectangular, beaded cells and stomata; (2) *cortex* several cells thick; (3) *outer phloem* with bast fibers; (4) *xylem zone*; (5) *inner phloem*; and (6) *pith*.

Calyx (Fig. 123).—(1) *Outer epiderm* (*aep*) of rectangular or polygonal, beaded cells, numerous stomata, and short blunt unicellular hairs; (2) *outer hypoderm*, a close chlorophyll parenchyma; (3) *mesophyll*, a loose parenchyma, with crystal sand cells (*cr*), through which

run the bicollateral fibro-vascular bundles; (4) *inner hypoderm*; and (5) *inner epiderm* (*iep*) with multicellular, capitate, glandular hairs and short unicellular hairs.

Bast fibers (f^1) and *stone cells* (st^1) occur in the phloem. The *vessels* are spiral (*sp*), reticulated, and pitted. Accompanying them are *wood parenchyma*, *wood fibers* (f^2), and *stone cells* (st^2 , st^3).

Pericarp (Figs. 124, 125, and 126).—This consists of (1) *epicarp* (*epi*) of polygonal, beaded cells with thick grooved cuticle; (2) *hypoderm* (*col*) of several rows of collenchymatously thickened, beaded cells; (3) *outer mesocarp* (*mes*) of thick-walled, beaded cells; (4)

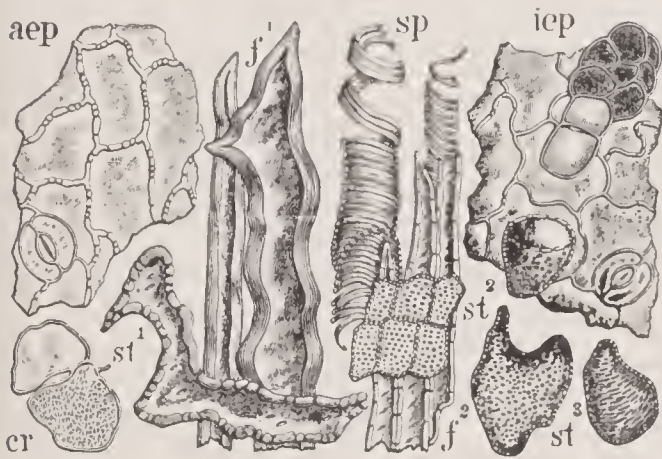


FIG. 123.

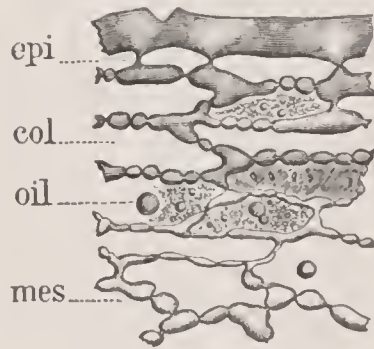


FIG. 124.

FIG. 123.—Paprika. Elements of calyx in surface view. *aep* outer epiderm; *cr* crystal sand cell of mesophyl; f^1 bast fibers and st^1 stone cells of bast; *sp* spiral vessels, f^2 wood fibers, st^2 , st^3 stone cells of bundle; *iep* inner epiderm with capitate and unicellular hairs. $\times 160$. (K.B.W.)

FIG. 124.—Paprika. Outer pericarp in cross section. *epi* epicarp with v-shaped groove in outer wall; *col* collenchyma; *mes* outer mesocarp with *oil* oil drops. $\times 160$. (K.B.W.)

inner mesophyl of thin-walled ground parenchyma and fibro-vascular bundles; (5) *giant cells*, and (6) *endocarp* with thick- and thin-walled groups.

The grooves in the *cuticle* are evident in cross section and surface view. Molisch has shown that the cell walls in both epicarp and hypoderm give a yellow color with caustic alkali, hence are suberized or perhaps more correctly sclerenchymatized.

Throughout the hypoderm and mesocarp are present *oil drops* (*oil*) and red *chromoplasts*, the latter in water mounts coloring the oil drops orange red. Treated with concentrated sulphuric acid, they become indigo blue.

Starch grains occur in immature specimens.

Of particular interest is the chain of *giant cells* (see Cayenne, Fig. 129). These reach enormous size (over 2 mm.), appearing as blisters on the inner surface, and are bounded without by mesocarp cells, within by the sclerenchymatized endocarp cells, and on either side partly by adjoining giant cells and partly by triangular groups of small cells resting on the thin-walled cells of the endocarp.

The cells of the *endocarp* (Fig. 126) over the giant cells are sclerenchymatized and beaded (*scl*); over the triangular groups of cells they are thin-walled (*p*).

Dissepiments (Partitions.)—Both *epiderms* correspond with the endocarp of the pericarp proper. The cell walls in part are sclerenchymatously thickened and beaded. Arthur Meyer¹ discovered that



FIG. 125.

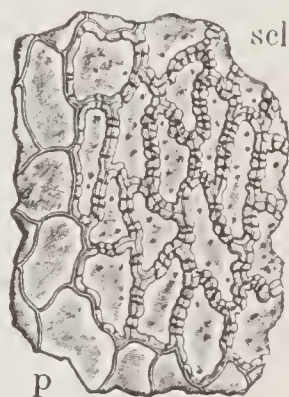


FIG. 126.

FIG. 125.—Paprika. Epicarp in surface view showing longitudinal grooves in cuticle. $\times 160$. (K.B.W.)

FIG. 126.—Paprika. Endocarp in surface view showing *scl* sclerenchyma cells, beneath giant cells, and *p* thin-walled cells. $\times 160$. (K.B.W.)

the seat of the pungent principle, *capsaicin*, is in cuticular blisters where it exists as tabular crystals dissolving in alkali with the formation of octahedral crystals.

Spermoderm.—Cross sections (Fig. 127, *S*) show three layers: (1) *outer epiderm* (*aep*) with outer wall of uniform thickness consisting of thin cuticle (*cut*), thicker cellulose lamella (*c*), and inner thin sclerenchyma lamella (*scl*), and with inner walls enormously thickened, folded, and warty (*w*); (2) *compressed parenchyma* (*p*); and (3) *inner epiderm* (*iep*) of thin-walled cells.

In surface view (Fig. 128) the side walls of the *outer epiderm* are sinuous and irregularly thickened with distinct warts on the inner wall.

¹ Pharm. Ztg. 1889, **34**, 130.

The *outer epiderm* is thickest at the edge of the seed where, seen in surface view, the walls are less sinuous but more warty than elsewhere.

Endosperm (Fig. 127, *E*).—Typical *aleurone cells* (*al*) with stiff but not very thick walls and small aleurone grains and fat make up a uniform tissue.

Embryo.—Thin-walled throughout with aleurone grains and fat as cell contents.

CHIEF STRUCTURAL CHARACTERS.—Fruit large, conical, two- to

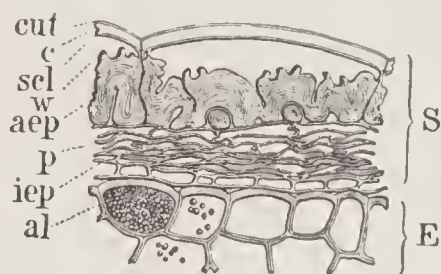


FIG. 127.



FIG. 128.

FIG. 127.—Paprika. Outer portion of seed from flat side in cross section. *S* spermoderm: *aep* outer epiderm with *cut* cuticle, *c* cellulose lamella, *scl* sclerenchyma lamella, and *w* warts; *p* parenchyma; *iep* inner epiderm. *E* endosperm: *al* aleurone cells. $\times 160$. (K.B.W.)

FIG. 128.—Paprika. Epiderm of spermoderm in surface view showing radial walls, thin above and irregularly thickened below, and warts covering inner wall. $\times 160$. (K.B.W.)

three-loculed. Seeds numerous, flattened, campylotropous, up to 5 mm. with embryo coiled in endosperm.

Epicarp cells polygonal, beaded, grooved; hypoderm with swollen beaded walls; mesocarp with oil drops and orange-red chromoplasts; giant cells 2 mm. or more; endocarp with groups of thick- and thin-walled cells. Outer epiderm of spermoderm with thick, folded, warty, porous, sclerenchymatized inner wall.

MICROSCOPY OF GROUND PAPRIKA.—See Cayenne Pepper.

CHEMICAL COMPOSITION.—Hungarian red pepper, or paprika, and Spanish red pepper, or pimiento, are treated in articles by Doo-

COMPOSITION OF PAPRIKA AND PIMIENTO

	In whole	Water	Protein	Oil, fixed	Oil, volatile	Starch equiv.	Fiber	Ash, total	Ash, soluble	Sand	Ash, alk.
	%	%	%	%	%	%	%	%	%	%	cc.
D. and O.											
<i>Paprika.</i>											
Whole:											
Min.	100	7.26	14.06	7.42	0.17	19.56	15.10	5.63	4.67	0.05	6.2
Max.	100	9.39	17.44	11.99	1.25	21.40	19.83	7.06	5.68	0.22	8.0
Aver. (6) .	100	8.54	15.43	9.30	0.85	20.44	15.31	6.28	5.12	0.10	7.1
Shells:											
Min.	57	9.45	12.50	4.01	0.44	22.16	16.66	5.50	4.85	0.03	5.9
Max.	64	10.86	15.37	6.69	1.10	24.52	23.61	6.90	6.10	0.08	8.6
Aver. (7) .	62	10.37	16.33	5.08	0.80	23.90	19.50	6.03	5.44	0.05	6.9
Seeds, etc.:											
Min.	26	5.00	16.56	17.66	0.95	17.36	17.29	3.06	1.72	0.05	3.4
Max.	40	6.46	21.19	22.34	1.90	18.16	20.11	4.93	3.72	0.09	6.8
Aver. (7) .	31	5.80	18.66	20.31	1.50	17.68	18.74	3.90	2.85	0.07	4.9
Stems:											
Min.	3	3.10	14.37	1.38	0.27	19.86	10.03	6.93	0.30	12.2
Max.	9	9.58	18.00	2.39	0.78	29.94	12.25	9.28	0.61	15.3
Aver. (7) .	7	6.55	15.87	1.94	0.48	24.47	11.32	8.36	0.44	14.1
<i>Pimiento.</i>											
Whole:											
Min.	100	8.28	14.62	10.39	1.18	16.52	15.37	5.24	4.59	0.05	6.1
Max.	100	8.58	16.87	10.39	1.18	16.52	15.37	6.79	5.79	0.06	7.9
Aver. (2) .	100	8.43	15.75	10.39	1.18	16.52	15.37	6.02	5.19	0.05	7.0
Shells:											
Min.	6.26	11.64	4.48	0.51	19.96	14.80	6.23	5.70	0.05	7.7
Max.	10.35	14.06	4.76	1.40	19.96	15.19	7.68	6.68	0.20	8.9
Aver. (3) .	55	7.69	13.05	4.62	0.95	19.96	15.00	7.17	6.22	0.11	8.5
Seeds, etc.:											
Min.	5.19	15.50	18.99	1.56	16.12	19.48	3.41	2.23	0.04	1.8
Max.	6.58	16.25	19.80	2.25	16.12	24.01	5.20	4.35	0.11	3.0
Aver. (3) .	36	5.74	15.92	19.40	1.91	16.12	21.74	4.41	3.37	0.06	2.3
Stems:											
(Aver.) .	9	4.74	11.56	0.98	0.29	29.99	15.50	13.09	0.26	14.1
T. and M.											
<i>Paprika.</i>											
Whole:											
Min.	100	3.29	12.21	0.08	20.69	5.08	0.24	...
Max.	100	3.76	16.43	0.89	22.76	6.03	0.33	...
Aver. (7) .	100	3.47	14.04	0.42	21.93	5.63	0.28	...
Shells:											
Min.	51	3.44	5.14	0.16	22.20	6.29	0.22	...
Max.	64	4.00	6.90	0.44	24.07	7.11	0.37	...
Aver. (7) .	56	3.63	6.07	0.28	23.19	6.60	0.28	...
Seeds, etc.:											
Min.	28	3.73	25.97	0.00	20.89	3.38	0.21	...
Max.	43	4.23	27.56	0.15	21.60	3.80	0.30	...
Aver. (7) .	36	3.97	26.96	0.06	20.76	3.63	0.26	...
Stems:											
Min.	6	4.66	2.11	0.15	29.34	9.84	0.66	...
Max.	9	5.78	3.05	0.35	32.86	11.35	1.20	...
Aver. (7) .	8	5.22	2.54	0.23	30.67	10.59	0.85	...
<i>Pimiento.</i>											
Whole:											
Min.	100	4.31	11.30	0.10	19.53	6.98	0.29	...
Max.	100	5.98	12.58	0.69	20.59	7.86	0.48	...
Aver. (7) .	100	5.06	11.87	0.47	20.13	7.39	0.35	...
Shells:											
Min.	53	4.74	5.44	0.41	17.26	7.50	0.26	...
Max.	58	5.02	6.81	1.05	18.70	8.46	0.37	...
Aver. (8) .	56	4.83	6.30	0.71	18.04	7.99	0.32	...
Seeds, etc.:											
Min.	35	3.59	21.82	0.05	19.90	4.43	0.22	...
Max.	37	4.12	24.58	0.42	24.08	5.02	0.31	...
Aver. (8) .	36	3.92	23.10	0.21	22.37	4.79	0.27	...
Stems:											
Min.	6	4.86	1.22	0.15	27.66	13.00	0.58	...
Max.	11	5.98	2.05	0.49	30.98	15.77	1.07	...
Aver. (8) .	9	5.35	1.44	0.31	29.43	14.53	0.73	...

little and Ogden,¹ Lowenstein and Dunne,² and Tolman and Mitchell.³ The table here given shows only the usual proximate constituents as summarized from the first and third papers. The figures in the column headed Water are not strictly comparable since Doolittle and Ogden determined the total loss at the temperature of boiling water and Tolman and Mitchell determined the loss at 70° *in vacuo*. The alkalinity of the ash is expressed in terms of cc. *N*/10 acid per gram of sample. For explanation of the other constituents see Cayenne Pepper. Data on the values of the ether extract, by the same authors, appear under Fixed Oil.

An analysis of Silesian Spanish pepper by Peyer, Hoffmann, and Schölzel⁴ gave: loss at 100° C. 6.50, protein 15.21, non-volatile ether extract 6.40, volatile ether extract 1.05, petroleum ether extract 5.65, alcohol extract 36.90, capsanthin 2.05, ash 7.60, and sand 0.04 per cent.

The *U. S. Standards* require that paprika not otherwise designated contain not more than 8.5 per cent of total ash and 1 per cent of sand, also that the iodine number of its extracted oil be between 125 and 136. They further give the following maximum limits respectively for (1) ground Hungarian rose paprika (Rosenpaprika, rozsapaprika) prepared from specially selected pods with removal of placentæ, stalks, and stems; (2) Hungarian king's paprika (Koenigspaprika) prepared without selection and including seeds and stems naturally occurring with the pods; and (3) Spanish paprika (pimenton, pimienta): non-volatile ether extract 18, 18, and 18, fiber 23, 23, and 21, total ash 6, 6.5, and 8.5, and sand 0.4, 0.5, and 1 per cent.

Changes in Composition During Growth.—Sievers and McIntyre⁵ traced the changes in composition of a variety of *C. annuum* L., denominated paprika, grown at Arlington, Va., through six stages beginning when the pod was green, less than 25 mm. long, and weighed 1.89 grams, to when the pod was dark red, exceeded 100 mm. in length, and had begun to lose in weight from the maximum of 14.86 grams. The results are of special interest because of the progressive increase of the fixed and volatile oils and of reducing sugars, and the decrease in ash.

¹ J. Am. Chem. Soc. 1908, **30**, 1481.

² J. Ind. Eng. Chem. 1910, **2**, 139.

³ Ibid. 1913, **5**, 747.

⁴ Deut. Apoth.-Ztg. 1937, **52**, 799.

⁵ J. Am. Chem. Soc. 1921, **43**, 2101.

CHANGES IN COMPOSITION DURING GROWTH (SIEVERS AND MCINTYRE)

Stage	Water	Oil, fixed	Oil, volatile	Alcohol extract	Sugar, total	Sugar, reducing	Ash
	%	%	%	%	%	%	%
1	8.46	1.95	0.19	18.72	11.90	5.81	8.13
2	6.79	2.47	0.17	17.03	13.81	5.81	7.72
3	7.63	4.82	0.22	18.25	14.72	6.27	7.57
4	7.19	5.24	0.27	19.15	13.92	5.90	7.00
5	7.21	6.35	0.24	19.24	13.32	6.42	6.85
6	7.16	8.33	0.85	21.15	14.39	8.59	6.78

Fixed Oil.—Doolittle and Ogden ¹ determined the iodine number of the fixed oil as obtained in the regular proximate analysis with the view of establishing limits that would serve in the detection of oil added to intensify the color of the spice. Soon after, cooperative experiments made by members of the Association of Official Agricultural Chemists failed to secure concordant results by the usual method, owing doubtless to differences in the amounts of oil extracted and different degrees of oxidation of the oil during drying at 105° C.

Winton,² proposed a shaking method of extraction, similar to that used for alcohol extraction, and Seeker ³ limited the time to 2 hours, shaking every 30 minutes (later to 1 hour shaking every 20 minutes), and after distilling off the ether limited the drying of the oil at the temperature of boiling water to 30-minute periods. By this process the extract was 1 to 2 per cent lower than by continuous extraction and the results on iodine number were more uniform. It is not improbable, however, that the small amount of oil added would be masked by variations in the normal products.

Tolman and Mitchell ⁴ used this method in the examination of the samples on which proximate analyses had been made as summarized above. See table on next page. For uniformity the refractive indexes given in the original at 40° have been reduced to 25° C. by adding the arbitrary correction of 0.00036 for each degree.

Lowenstein and Dunne ⁴ obviated oxidation of the oil, obtained by continuous extraction, by drying *in vacuo*, but their results show wider variation than those of Tolman and Mitchell.

¹ Loc. cit.

² U. S. Dept. Agr., Bur. Chem. 1909, Bul. **122**, 38.

³ Ibid. 1910, Bul. **132**, 114.

⁴ Loc. cit.

	Per cent of oil			Ref. index 25° C.			Iodine No. (Hanus)		
	Whole	Shells	Seeds	Whole	Shells	Seeds	Whole	Shells	Seeds
Paprika:									
Min.....	10.86	4.14	22.53	1.4812	1.4745	129.8	133.2	133.1
Max.....	15.00	5.26	24.96	1.4908	1.4753	134.0	149.5	134.0
Aver.....	12.61	4.68	23.53	1.4860	1.4750	132.6	140.1	133.5
Pimiento:									
Min.....	9.81	4.26	19.11	1.4830	1.5012	1.4749	136.0	136.7	128.1
Max.....	10.81	4.67	21.35	1.4872	1.5022	1.4756	137.3	143.7	130.8
Aver.....	10.34	4.46	19.99	1.4859	1.5017	1.4753	136.7	141.0	129.9

Determination by v. Sigmond and Vuk ¹ of percentage of parts of the fruit in the whole fruit of Hungarian paprika, of oil (ether extract) in the parts, and iodine number of the oil gave respectively: pericarp 58, 14.8, and 133.9; seeds 32, 32.09, and 139.9; placentas 4.5, 13.81, and 133.6; stems 5.5, 2.54, and 111.3. Spanish peppers both sweet and sharp contained 41 per cent of seeds.

Extraction of the dried seeds of sweet peppers by Comanducci and Tomasini ² gave 25.7 per cent of oil with the following values: specific gravity at 15° C. 0.922; refractive index (recalculated) 1.47; Maumené number 89°; solidifying point 12° C.; saponification number 184.6; iodine number "relative" 129, "absolute" 141.3; Reichert-Meissl number 17.3; Hehner number 85.4; acetyl number 39.96; solid fatty acids 32 per cent; liquid fatty acids 68 per cent; melting point of solid acids 40 to 43° C.; hydroxy acids 1.64 per cent; and acid number 11.28 per cent.

Ebert and Bailey,³ in expressed oil from seeds of a Georgia cannery after refining, bleaching, and deodorizing, secured the following figures: specific gravity 15°/15° (recalculated) 0.9260, refractive index at 25° C. (recalculated) 1.4732, saponification number 171.4, iodine number (Wijs) 134.4, saturated acids 12.6, unsaturated acids 82.8, iodine number of unsaturated acids 157.9, and free fatty acids 0.03 per cent. The seed contained 18.2 per cent of oil.

Volatile Oil.—By the Von Fellenberg chromic acid oxidation method, Zäch ⁴ obtained 0.5 to 1.0 per cent.

¹ Z. Unters. Nahr.-Genussm. 1911, **22**, 599.
² Rend. accad. sci. Napoli 1921, **27**, 38.
³ Cotton Oil Press 1924, **7**, 35.
⁴ Mitt. Lebensm. Hyg. 1932, **23**, 156.

Capsaicin.—Thresh¹ first isolated this substance and gave it its name but gained no insight into its constitution. Analyses of his preparation by Flückiger and Buri² suggested the formula $C_9H_{14}O_2$ but showed no nitrogen.

Micko,³ overcoming the difficulties of previous investigators, prepared from paprika a considerable amount of the pure crystalline substance melting at 63.5° C. Analysis indicated the formula $C_{18}H_{28}NO_3$. He showed that the substance was a phenol with an hydroxyl and a methoxyl group. Furthermore he noted an odor of vanillin when a mixture of an alcoholic solution of capsaicin, platonic chloride solution, and hydrochloric acid was allowed to evaporate spontaneously. The formation of a double platinum salt, even when the amount of capsaicin was minute, was the only characteristic chemical reaction noted. Micko states, however, that the sense of taste is the most delicate test, since a single drop of a 0.001 per cent alkaline water solution produces a sharp burning taste on the tongue. The crude capsaicin isolated indicated the presence of about 0.03 per cent in the spice. Later⁴ he separated from cayenne pepper an amount of the crude substance equivalent to 0.55 per cent.

The same author prepared benzoyl capsaicin which melted at 74° C. and was not pungent.

Nelson,⁵ following Micko's method, prepared from "African capsicum" a quantity of pure capsaicin melting at 64.5° C. equivalent to 0.14 per cent of the spice. For later experiments⁶ he prepared from cayenne pepper crude and pure capsaicin representing respectively: 0.34 and 0.22 per cent of the pepper. His experimental work comprised the preparation of methyl capsaicin, its oxidation and acid hydrolysis, acid hydrolysis of capsaicin, synthesis of vanillyl-amine, and alkaline hydrolysis of capsaicin. He concludes that capsaicin is a condensation product of vanillyl-amine and a decylenic acid and gives empirical and structural formulas. His empirical formula $C_{18}H_{27}\underline{NO_3}$ differs from that of Micko in having one less hydrogen.

Acids.—Compared with other vegetable products, paprika, according to Svirbely and Szent-Györgyi,⁷ is rich in *ascorbic acid*, which they consider is identical with vitamin C. From 500 grams of peppers

¹ Pharm. J. Trans. 1876-77, 7, 21, 259, 473; 1877-78, 8, 187.

² J. Forts. Pharmakog. 1876.

³ Z. Unters. Nahr.-Genussm. 1898, 1, 818.

⁴ Ibid. 1899, 2, 411.

⁵ J. Ind. Eng. Chem. 1910, 2, 419.

⁶ J. Am. Chem. Soc. 1919, 41, 1115.

⁷ Biochem. J. 1933, 27, 279.

of a variety of *Capsicum annuum* L., Spruyt and Van Veen¹ isolated 100 mg. of crystallized ascorbic acid. Fernández and Alfageme² obtained the following results: green pimento 1250, red pimento 2360, and paprika 1060 mg. per kilo, fresh basis.

Sugiura³ observed that during ripening of Manchurian paprika (*C. annuum* L., var. *grossum* Sendt.) the ascorbic acid increases; during storage, exposure to air after rubbing, or other oxidizing agents it decreases. At maturity the ratio of ascorbic acid to glutathione (absent in green fruit) is 1 : 1.7. For 3 varieties grown in 19 districts of Manchuria he⁴ reports a content of 730 to 3000 mg. per kilo of ascorbic acid.

Carbohydrates.—In the pericarp of paprika grown in Kalocsa, Hungary, Tompos⁵ found in July *reducing sugar* (Calculated as dextrose) 1.15 to 1.73 and *sucrose* 0.09 to 1.15 and in September *reducing sugar* 5.53 to 5.82 and *sucrose* 0.55 to 0.61 per cent, fresh basis.

Pentosans.—In dry matter 8.28 per cent. See also Introduction to Part III.

Colors. *Capsanthin*, $C_{40}H_{58}O_3$.—From a low-boiling petroleum ether extract of paprika pericarp, Zechmeister and v. Cholnoky⁶ isolated capsanthin in the form of deep carmine or light brick-red crystals with a blue-black luster, melting at 167 to 168° C., at first assigned the formula $C_{34}H_{48}O_3$ or $C_{34}H_{50}O_3$. The dried material was estimated to contain about 0.4 per cent. The yield was 0.12 to 0.33 per cent. In a more recent investigation,⁷ the melting point 175 to 176° C. and the formula $C_{40}H_{58}O_3$ were established. Brown⁸ concluded that the pigment of Perfection red peppers is capsanthin. Although Bilger⁹ believed that the pigment of Japan pepper is not the same as that of paprika, Zechmeister and v. Cholnoky¹⁰ present evidence to the contrary.

From an alcoholic solution of capsanthin, by treatment with potassium hydroxide and purification, Zechmeister and v. Cholnoky¹¹ iso-

¹ Geneeskund Tijdschr. Nederland. Indie 1936, **76**, 1065.

² Rev. sanid. hig. pub. 1936, **11**, 525.

³ J. Orient. Med. 1936, **25**, 37.

⁴ Ibid. 1938, **28**, 175.

⁵ Kísérletügyi Közlemények 1934, **37**, 286.

⁶ Ann. 1927, **454**, 54.

⁷ Ibid. 1934, **509**, 269.

⁸ J. Biol. Chem. 1935, **110**, 91.

⁹ Bul. Basic Sci. Res. 1931, **3**, 37.

¹⁰ Ann. 1931, **489**, 1.

¹¹ Ann. 1937, **530**, 291.

lated 16 per cent of *citraurin* identical with that present in orange peel. Zeaxanthin and β -carotene are not changed by this treatment.

In the pericarp of ripe paprika and of the capsaicin-free variety respectively, Cholnoky¹ found: capsanthin 0.219 to 0.349 and 0.079 to 0.319; capsorubin 0.042 to 0.098 and 0.017 to 0.062; total pigments 0.407 to 0.549 and 0.176 to 0.520 per cent.

Carotene.—After removal of the capsanthin, the above authors isolated carotene. The dried material contained about 0.04 per cent and was then thought to be a suitable raw material for the preparation of the color, but later only a small amount was found. Brown² separated from the dried shell of the Perfection variety 0.02 to 0.067 per cent of what he believed was the β -form of carotene.

Capsorubin, zeaxanthin, cryptoxanthin, and in some samples *lutein* (xanthophyl) were identified by Zechmeister and v. Cholnoky.³ The pigment with the absorption bands of lycopersicin, isolated by Duggar⁴ from red peppers, may have been one of the four named above or a mixture.

Color Values.—Varga⁵ notes the difference in the color combinations in different varieties as determined by the Ostwald method.

Mineral Constituents.—Mehring,⁶ who has compiled numerous analyses of spices, gives 6.78 per cent as the average ash content of 449 samples, as determined by 12 analysts, and the following analysis of the ash:

K ₂ O	Na ₂ O	CaO	MgO	Fe ₂ O ₃	Al ₂ O ₃	CuO	P ₂ O ₅	SO ₃	SiO ₂	Cl
%	%	%	%	%	%	%	%	%	%	%
54.37	3.98	5.15	6.02	1.97	0.09	0.10	16.43	5.70	2.68	3.51

Pericarps of first and second quality, as determined by Tompos,⁷ contained respectively: ash, 5.67 to 6.47 and 7.66 to 9.22, sand 0.005 to 0.013 and 0.020 to 0.073 per cent. The first, second, and third quality ground product contained ash 5.04 to 5.28, 7.07, and 7.89, and sand 0.006, 0.039, and 0.042 per cent.

¹ Kísérletügyi Közlemények 1937, **40**, 173.

² Science 1934, **79**, 481.

³ Ann. 1934, **509**, 269.

⁴ Washington Univ. Studies 1913, **1**, 22.

⁵ Z. Unters. Lebensm. 1930, **60**, 268.

⁶ J. Agr. Res. 1924, **29**, 569.

⁷ Kísérletügyi Közlemények 1935, **38**, 262.

Sarudi¹ determined the pure ash in the dry matter and analyzed the pure ash of the fruit walls with and without removal of the offal (stems and placenta), of the seeds both washed and unwashed, and of four commercial grades, belonging to a different classification from that previously given, with results as follows:

	Ash	K ₂ O	Na ₂ O	CaO	MgO	Fe ₂ O ₃	Al ₂ O ₃	P ₂ O ₅	SO ₃	Cl	SiO ₂
	%	%	%	%	%	%	%	%	%	%	%
Parts:											
Walls only.....	5.50	62.14	2.09	2.52	3.74	0.69	0.47	13.20	9.20	4.04	1.75
Walls and offal..	6.80	71.40	3.51	1.74	3.27	0.26	0.33	9.02	5.43	3.63	1.68
Seeds, washed...	2.94	21.64	2.10	10.48	15.70	1.02	0.00	38.66	9.50	0.31	0.58
Seeds, unwashed.	4.19	32.93	1.79	2.88	11.92	0.88	0.16	31.57	15.27	2.85	0.75
Grades:											
Sweet-delicate...	5.35	60.35	1.61	5.70	6.41	0.54	0.34	14.33	6.63	3.74	1.31
Sweet.....	5.37	56.41	1.69	3.93	6.63	0.61	0.26	16.13	6.72	4.73	3.00
Rose.....	5.86	52.55	3.07	4.71	6.54	0.74	0.75	15.56	7.42	3.61	5.05
Sharp.....	5.70	53.62	2.01	5.41	7.38	1.09	0.47	16.81	6.51	2.90	4.53

CAYENNE PEPPER

Capsicum frutescens L.

Fr. Poivre de Cayenne. Sp. Picante. It. Pepe di Caienna.

Ger. Cayennepfeffer.

No little confusion exists as to the nomenclature of the plants furnishing the small-fruited, highly pungent red peppers known as cayenne pepper or chillies. The species named above unquestionably is one, if not the only, species. *C. baccatum* L. is mentioned by some authors, but this with reason is regarded by Irish as a variety of *C. frutescens*, which view places it on the same plane as numerous varieties not provided with Latin names. It is uncertain whether *C. fastigiatum* Bl. and *C. minimum* Roxb., often mentioned as yielding cayenne pepper, are distinct species, or even varieties, and even if distinct it is doubtful whether either furnishes any considerable amount of the commercial product. It is not improbable, however, that the plant yielding the so-called Bombay cherry capsicum is a distinct variety or species, since the histology of the fruit in some details is distinct from that of the fruit of either *C. annum* or *C. frutescens*.

In view of the confusion caused by attempting to classify peppers as paprika and cayenne according to size of the fruit or the botanical

¹ Z. Unters. Lebensm. 1938, 74, 292.

species or variety, it would seem rational to adopt simpler names such as mild red pepper and hot red pepper.

Figure 122 shows a fruit of Zanzibar chillies, one of the common grades. These as well as Sierra Leone and Mombassa chillies are of a dull red color.

MACROSCOPIC STRUCTURE.—Except for the smaller size of the parts, the general structure is like that of paprika.

MICROSCOPIC STRUCTURE. Peduncle and Calyx.—Practically as in paprika.

Pericarp.—Distinctions from paprika lie in the form and arrange-

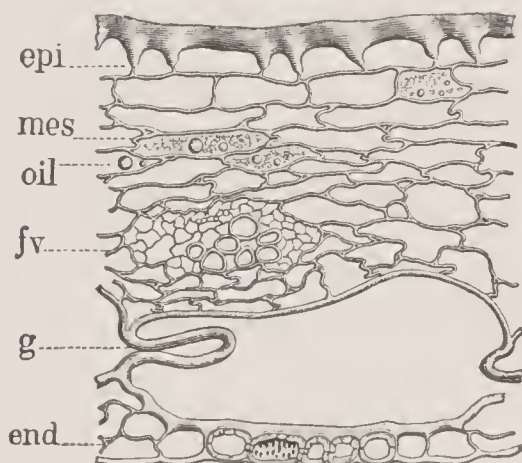


FIG. 129.

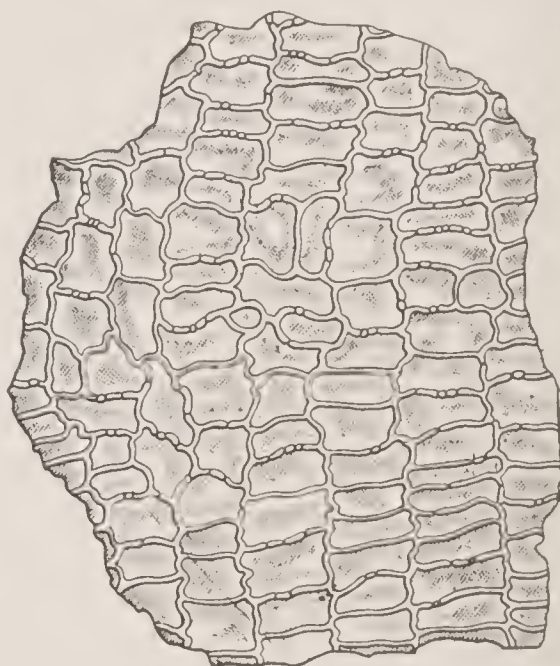


FIG. 130.

FIG. 129.—Cayenne Pepper. Pericarp in cross section. *epi* epicarp; *mes* mesocarp with *oil* oil drops and *fv* bundle; *g* giant cells; *end* endocarp. $\times 160$. (K.B.W.)

FIG. 130.—Cayenne Pepper. Epicarp in surface view. $\times 160$. (K.B.W.)

ment of the epicarp cells and the absence of a hypodermal layer of collenchymatously thickened, sclerenchymatized cells.

The *epiderm* (Fig. 129, *epi*; Fig. 130) consists of more or less quadrilateral, faintly beaded cells, arranged in distinct longitudinal rows, not as in paprika of polygonal and irregularly arranged cells. Cuticular grooves are not evident.

The abrupt transition from epicarp to thin-walled mesocarp is shown in cross section.

Spermoderm (Fig. 131, *S*; Fig. 133).—The *outer epiderm* differs from that of paprika in that (1) the sclerenchyma lamella of the outer

wall, as seen in cross section, is relatively thicker, about equaling the cellulose lamella, and (2) the inner wall, as seen in both cross section and surface view, is not warty.

No difference in the remaining layers is noticeable.

Endosperm (Fig. 131, *E*) and **Embryo**.—As in paprika.



FIG. 131.

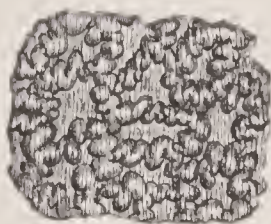


FIG. 132.

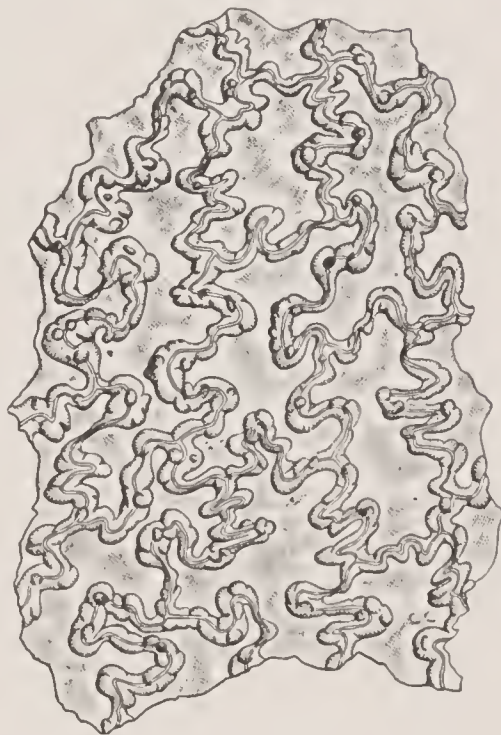


FIG. 133.

FIG. 131.—Cayenne Pepper. Outer portion of seed from flat side in cross section. *S* spermoderm: *aep* outer epidermis with *cut* cuticle, *c* cellulose lamella, and *scl* sclerenchyma lamella; *p* compressed parenchyma; *iep* inner epidermis. *E* endosperm with *al* aleurone cells. $\times 160$. (K.B.W.)

FIG. 132.—Bombay Capsicum. Epicarp in surface view. $\times 160$. (K.B.W.)

FIG. 133.—Cayenne Pepper. Outer epidermis of spermoderm in surface view. $\times 160$. (K.B.W.)

CHIEF STRUCTURAL CHARACTERS.—Fruit small but general structure as in paprika.

Epicarp cells quadrilateral in rows (in paprika, polygonal, irregularly arranged); cuticular grooves absent (in paprika present). Outer wall of outer epidermis of spermoderm with thicker sclerenchyma lamella than in paprika, inner wall not warty (in paprika warty).

MICROSCOPY OF GROUND CAYENNE PEPPER.—Brick dust, red sawdust, and various cereal powders dyed red have been reported as adulterants. Sawdust may be detected by the characteristic wood

tissues, cereal products by the starch and bran tissues described in Volume I.

CHEMICAL COMPOSITION.—The following table, showing results on chillies or cayenne pepper by Winton, Ogden, and Mitchell,¹ Tolman and Mitchell,² and Boyles,³ is chiefly of interest to the forensic chemist. The nature and amount of the flavoring principle are not indicated.

COMPOSITION OF CHILLIES (CAYENNE PEPPER)

	Water	Protein	Oil, fixed	Oil, volatile*	Alcohol extract	Pure starch†	Starch equiv.‡	Fiber	Ash, total	Ash, soluble	Sand
	%	%	%	%	%	%	%	%	%	%	%
W. O. and M.											
Zanzibar:											
Min.	3.67	13.31	15.63	0.56	19.92	0.84	8.91	23.44	5.24	3.30	0.11
Max.	6.87	14.62	19.11	2.57	25.64	1.46	9.31	27.65	6.13	4.29	0.19
Aver. (4) . .	5.15	13.80	17.57	1.59	22.58	0.76	9.09§	25.09	5.60	3.59	0.16
Japan:											
Min.	5.61	13.44	20.89	0.78	23.19	0.80	7.15	21.44	5.18	4.17	0.05
Max.	6.45	14.63	21.81	1.16	25.46	1.46	8.19	21.95	5.96	4.93	0.14
Aver. (3) . .	5.95	13.94	21.28	0.99	24.11	1.20	7.66	21.68	5.65	4.55	0.09
T. and M.											
Mombassa:											
Min.	15.88	0.28	24.98	5.34	0.44
Max.	19.00	1.72	28.70	8.41	3.03
Aver. (27)	17.26	0.81	26.86	6.31	1.24
Japan:											
Min.	17.10	0.09	22.82	5.08	0.31
Max.	23.21	1.59	25.96	6.20	1.07
Aver. (17)	19.94	0.56	24.25	5.52	0.53
Boyles											
Mombassa:											
Min.	15.75	0.15	22.63	4.36	0.35
Max.	25.49	0.32	30.45	9.40	1.77
Aver. (7)	20.06	0.23§	26.25	6.08	1.06
Japan.	22.50	24.02	4.63	0.18

* Volatile ether extract. † Diastase method. ‡ Reducing matter, after washing with 10% alcohol and direct inversion of residue, calculated as starch. § 3 samples.

The *U. S. Standards* specify that cayenne pepper or cayenne is the dried ripe fruit of *C. frutescens* L., *C. baccatum* L., or some other small-fruited species of *Capsicum* and contains not less than 15 per cent of non-volatile ether extract and not more than 1.5 per cent of

¹ Connecticut Agr. Exp. Sta. Rep. 1898, p. 184; 1899, p. 100.

² J. Ind. Eng. Chem. 1913, 5, 747.

³ Ibid. 1917, 9, 301.

starch, 28 per cent of fiber, 8 per cent of total ash, nor 1.25 per cent of sand.

Fixed Oil, Capsaicin, Color.—See Paprika.

Pentosans.—In dry matter 8.57 per cent. See also Introduction to Part III.

CAPSICUMS

Capsicum spp.

Dried peppers of different shapes, sizes, shades of red or orange, and degrees of pungency are used for the preparation of ground red pepper and labeled paprika or cayenne according to the pungency of the powder. Some of these are doubtless the fruit of *C. annuum*, others of hybrids, but it is quite impossible to determine the botanical origin of products so varied in character and from such widely different regions.

Pods of some of the capsicums and chillies on the American market are shown in Fig. 122. Others not illustrated are Louisiana capsicums, similar to South Carolina capsicums, both being often broader than the pod of the latter illustrated, and Louisiana chillies with shorter and narrower pods. Japan chillies are smaller fruited, lustrous, and of a particularly brilliant red color.

Examination of the above-described varieties made by the authors brought out marked differences in structure as shown by the following classification.

Paprika type throughout: Japan chillies, Naples chillies, Louisiana capsicums (1 sample each). A second sample of Naples chillies had no warts on the inner wall of the outer epiderm of the spermoderm.

Pericarp of paprika type, spermoderm of cayenne type: South Carolina capsicums (1 sample).

Cayenne type throughout: Small Bombay capsicums (1 sample).

The remainder of the samples agreed in having a collenchymatously thickened hypoderm layer, as in paprika, but disagreed widely in other respects as follows:

Epicarp of cayenne type, spermoderm of paprika type: South India capsicums (2 samples). Large Bombay capsicums, and Bombay cherry capsicums (1 sample each) would fall in this class were it not that no warts were found on the inner wall of the outer epiderm of the spermoderm. Louisiana chillies (1 sample) had grooves on the epicarp but otherwise conformed to this class.

Some of the above samples, especially the South India capsicums

and Bombay cherry capsicums (Fig. 132), had walls of the epicarp strongly convoluted and striated instead of beaded.

Following the common classification, which groups large-fruited species under paprika and small-fruited species under cayenne, Japan chillies would pass as cayenne; in structure, however, they resemble Hungarian paprika. On the other hand, some of the larger-fruited sorts, such as Bombay capsicums, agree more nearly with cayenne in structure.

While Hungarian and Spanish paprika are readily distinguished from true cayenne, it is obvious that other commercial varieties are difficult to classify from their structure, and their indiscriminate use in the ground form introduces complications not readily cleared by microscopical examination.

CHEMICAL COMPOSITION.—Analyses by Winton, Ogden, and Mitchell¹ and by Boyles² of various large or medium podded hot peppers are grouped here under the general term Capsicums. As in other red peppers, the quality and composition vary greatly from year to year. The South Carolina capsicums were grown under the indirect supervision of the U. S. Bureau of Plant Industry from Hungarian paprika seed, but in the new habitat they developed such biting characters as to put them commercially in the class with capsicums.

Winton, Ogden, and Mitchell also determined the alcohol extract in Bombay capsicums with the following results: 24.42 and 27.61 per cent.

Roca³ gives the proximate composition of the dried fruit of chillies as follows: protein 18, fat 2.7, oleoresin 17, dextrose 4.3, starch 4, and ash 4.5 per cent, also a trace of an alkaloid, and coloring matter consisting chiefly of carotene and xanthophyl with a little lycopene or lycopersin. They consider that the flavoring matter consists of an unknown constituent of the resins, decenovannillylmethylamide, and related substances.

Fixed Oil, Capsaicin, Colors.—See paprika.

¹ Connecticut Agr. Exp. Sta. Rep. 1898, p. 184.

² J. Ind. Eng. Chem. 1917, 9, 301.

³ Anal. inst. biol. (Mexico) 1935, 6, 201.

COMPOSITION OF CAPSICUMS

	Sam- ples*	Water	Pro- tein	Oil, fixed	Oil, vola- tile†	Pure starch‡	Starch equiv.§	Fiber	Ash, total	Ash, solu- ble	Sand
		%	%	%	%	%	%	%	%	%	%
W. O. and M.											
Bombay:	2										
I.....		7.08	13.56	21.16	0.73	0.84	8.95	20.69	5.15	4.13	0.20
II.....		5.48	13.38	21.56	1.34	1.06	8.55	20.35	5.08	4.02	0.23
Boyles											
Bombay:	35										
Min.....		12.35	0.25	25.00	5.56	...	0.14
Max.....		20.40	0.72	32.30	9.35	...	1.75
Aver.....		16.57	0.45	28.08	6.95	...	0.76
Bombay cherries:	2										
I.....		15.60	29.20	5.35	...	0.65
II.....		17.55	0.30	27.45	5.67	...	0.82
S. Carolina:	17										
Min.....		4.40	10.75	0.15	20.07	4.82	...	0.25
Max.....		7.38	15.70	1.85	30.48	7.75	...	1.20
Aver.....		5.90	13.92	0.60	25.48	5.98	...	0.78
Japan:	19										
Min.....		12.80	0.30	22.50	4.90	...	0.14
Max.....		17.03	0.40	26.64	6.84	...	1.17
Aver.....		15.56	0.35	23.84	6.05	...	0.39
Korean:	4										
Min.....		19.77	0.45	25.85	6.20	...	0.20
Max.....		22.25	0.60	26.02	7.70	...	0.75
Aver.....		21.01	0.53	25.94	6.94	...	0.51
Niger:	3										
Min.....		18.22	0.25	22.82	5.27	...	0.60
Max.....		21.96	0.85	27.77	6.17	...	1.27
Aver.....		19.53	0.55	24.93	5.72	...	0.83
African:	1										
		19.45	28.76	5.05	...	0.95

* Fixed and volatile oil and fiber not determined in all the samples. † Volatile ether extract.
‡ Diastase method. § Reducing matter, after washing with 10% alcohol and direct inversion of
residue, calculated as starch.

PART IV
LEAVEN

PART IV

LEAVEN

THE term leaven or leavening is deemed sufficiently comprehensive to cover all sources of carbon dioxide used in raising bread, cake, and related cereal products. Yeast may be defined as *biological leaven* and sodium bicarbonate and baking powder containing it as *chemical leaven*. The simplest chemical leaven is *sodium bicarbonate*, which is effective when added alone if the dough or batter contains an acid-reacting ingredient such as sour milk, molasses, or chocolate, or when added in conjunction with cream of tartar or other acid-reacting chemical. At the present time, however, sodium bicarbonate is more commonly used in the form of *baking powder* containing an amount of acid-reacting chemical sufficient to liberate the carbon dioxide.

YEAST

Yeast is an ancient food accessory. The loaves buried with Egyptian mummies and those dug up in Pompeii were made with yeast. So desirable is yeast bread that the term "unleavened" carries with it the idea of penance. When slow methods of fermentation were practiced, yeast was a minor addition to the loaf; now, however, when time is conserved by using larger amounts of yeast, the food value thus added is worthy of consideration. Yeast plays a still greater part in the day's intake of nutrients and vitamins if, as is often practiced, yeast cakes are eaten separately either raw or cooked. The flavor of cooked yeast, as subsequently noted, suggests animal origin. Again, yeast, being related botanically to the mushrooms, may be classed as a vegetable. Thus the minute unicellular yeast plant serves as bread, flesh, and vegetable.

Physiologically, the yeast plant breaks down vegetable carbonaceous food, consisting essentially of sugars, into alcohol and carbon dioxide with loss of energy, thus differing radically from the process

of photosynthesis of higher plants which builds up carbon compounds and stores up energy. In both processes, however, mineral nitrogen is utilized in the synthesis of protein, which is never true of proteins formed by animals, but with the striking difference that the mineral nitrogen taken in by yeast is in the form of ammonium salts, whereas that taken in by higher plants, exclusive of the free nitrogen utilized by the legumes, is in the form of nitrate ready formed or formed from ammonia by nitrifying bacteria.

Manufacture of Yeast.—Even during the present generation, yeast was made in the household from potato mash. Emptyings, like glowing coals, were borrowed from neighbors when through accident the home supply was lost or had deteriorated. Commercially, yeast was a by-product from the brewing and distilling industries. Dry yeast cakes of the old days were dried mixtures of corn meal with yeast in the resting stage and water. They were made at home or on a commercial scale, as they still are to a limited extent.

The descriptions of the processes which follow are based on papers by Frey¹ and by Frey, Kirby, and Schultz,² all of the Fleischmann Laboratories, Standard Brands.

Vienna Process.—Compressed yeast was first made in the United States by Gaff, Fleischmann and Company at Cincinnati in 1868 and was exploited at the Centennial Exposition at Philadelphia, as some of us in advanced years well remember. The culture medium was unfiltered, unaerated malt and corn mash of 15 to 20° Balling. After 20 to 23 hours the yeast was skimmed off, washed, sifted from kernels, washed again, and pressed. By this process, a yield in terms of grain of 10 to 14 per cent of yeast and about 30 per cent of alcohol was secured. When aeration came into use, the yield of yeast went up to about double and that of alcohol down to nearly two-thirds. By further improvement in the process, notably by increasing the aeration and the dilution and lowering the temperature, the yield of yeast reached 40 per cent and that of alcohol was reduced to 15 per cent or less.

Hayduck Process.—In 1915 Hayduck revolutionized the manufacture by utilizing molasses, ammonia, and mineral salts, notably phosphates, as raw materials. The process was also modified. Starting with seed yeast and a dilute wort (1.5 to 2° Balling), the process was made continuous by gradually adding concentrated wort and ammonium hydroxide, the latter serving to obviate over-acidity as well

¹ Ind. Eng. Chem. 1930, **22**, 1154.

² Ibid. 1936, **28**, 879.

as to supply nitrogen as needed. A yield of 200 per cent in terms of the sugar in the wort may be secured with little or no formation of alcohol.

Nitrogenous Yeast Foods.—Pringsheim¹ discovered that the fermentative power of yeast is influenced by its nitrogenous food. Substances containing NH, CH, and CO in a chain, joined by single bonds and consequently having one bond free in each group, maintain the fermentative power. Examples are *asparagine*, *glutamine*, *leucine*, *glycocoll*, *alanine*, *tyrosine*, *hippuric acid*, *phenylalanine*, and *phenyl-aminoacetic acid*. *Uric acid*, with only C in the central group and consequently 2 free bonds, also acts favorably. Substances which act unfavorably are those with the following groups: =CH—CO—NH— , $\text{C}_6\text{H}_5\text{—CO—NH—}$, $\text{C}_6\text{H}_5\text{—NH—CO—}$, $\text{C}_6\text{H}_5\text{—CH}_2\text{—NH—}$. Other substances with good fermentative power, although not belonging to the foregoing classes, are *ammonium salts* and *urea* which may form ammonium carbonate.

The requirements of amino, particularly basic amino, nitrogen and peptide nitrogen, as well as total nitrogen, have been worked out by Pavcek, Peterson, Elvehjem, Saudek, Colingsworth, and Baldwin.²

Examination by Nielsen and Hartelius³ of 34 amino acids showed that only β -alanine, asparagine, aspartic acid, glutamic acid, lysine, and arginine acted as yeast stimulants and these only when in combined form. β -Alanine was most active, increasing growth 66 per cent on addition of 10% per cent.

Ehrlich⁴ grew normal yeast on a medium containing only mineral salts, sugar, and amino acids. Only ammonia derived from the amino acids was utilized by the yeast plant.

That yeast utilizes the nitrogen of *ammonium salts* was first shown by Duclaux⁵ and later verified by Pringsheim, Ehrlich, and others.

Nitrates were shown by Kossowicz⁶ to be unsuitable sources of nitrogen for yeast. Bokorny⁷ demonstrated that nitrates are not assimilable by yeast and simple *amines* are not suitable sources of nitrogen. The following increases in dry yeast were obtained in 2 days in various media: *ammonium sulphate* plus sucrose 71.8, *hydrazine sulphate* plus dextrose 113, *asparagine* plus sucrose 103.7, *aspartic acid*

¹ Ber. 1906, **39**, 4048.

² Wisconsin Agr. Exp. Sta. 1936, Bul. **435**, 80; 1937, Bul. **438**, 145; Bul. **439**, 59.

³ Biochem. Z. 1938, **295**, 211.

⁴ Biochem. Z. 1911, **36**, 477.

⁵ Ann. inst. Pasteur 1893, **7**, 751.

⁶ Biochem. Z. 1914, **67**, 400.

⁷ Chem. Ztg. 1916, **40**, 366.

plus sucrose 61.3, *leucine* plus sucrose 90.3, *tyrosine* 61.3, *glycine* 25.8, *peptone* plus sucrose 177.4, and *peptone* only 152 per cent. Flesh *albumose* caused a loss of 9.7 per cent, showing need of peptonizing.

Ivanov¹ worked on the decomposition of protein during autolysis and fermentation. In alkaline solution, an increase in *protein nitrogen* (Stutzer), at the expense of substances precipitated by phosphotungstic acid and lead acetate, was noted. However, after a time, a decrease in *ammonia nitrogen* without increase in protein nitrogen, due it was believed to formation of humin compounds, was observed. The formation of alcohol retards protein decomposition.

Classen² found that only 65 per cent of *malt extract nitrogen* is available for the growth of yeast and that only 40 per cent of this nitrogen can be replaced by ammonia nitrogen without causing a decrease in the yield.

In calculating the amount of ammonia salts essential for a desired yield of yeast from beet molasses, Ellrodt³ figures that 40 to 50 per cent of the nitrogen of the molasses is assimilable as compared with 25 per cent of grain or malt-combs and that 45 per cent of the dry matter of pressed yeast is protein. He supplements the phosphoric acid, of which only 0.6 per cent is present in molasses, by adding a suitable amount of superphosphate.

Classen⁴ reports yields of yeast with 25 per cent solids, grown with German beet molasses and added phosphoric acid, of 41 to 59 per cent, on the basis of molasses used. The utilization of nitrogen ranged from 40 to 60 per cent.

Only 40 per cent of the total nitrogen of beet molasses was found by Wohl⁵ available in yeast culture, 50 per cent by others. If, according to Classen,⁶ the optimum of ammonia is exceeded, little of the organic nitrogen is available. He states that Wohl does not distinguish organic soluble from effective nitrogen.

Storage.—Yeast deteriorates rapidly if stored at ordinary temperatures. Refrigeration during temperate and warm weather is imperative. Stored on ice, yeast, according to Larmour and Brockington,⁷ showed no significant change in leavening power for 19 days, then showed an increase up to the thirtieth day, followed by a decrease up

¹ Biochem. Z. 1921, **120**, 1, 25, 62.

² Z. angew. Chem. 1928, **41**, 1161.

³ Brennereizeit. 1918, **35**, 8183; 1919, **36**, 8239.

⁴ Z. Ver. deut. Zucker-Ind. 1926, **76**, 349.

⁵ Chem. Ztg. 1928, **52**, 202.

⁶ Ibid. p. 497.

⁷ Can. J. Research 1932, **6**, 614.

to the fifty-sixth day, ending with an activity greater than at the start.

Iwanowski and Brzezinski¹ attribute to fresh yeast the power of autofermentation. Albumin changes little up to liquefaction, the increase in soluble nitrogen being gradual. Hydrogen-ion concentration fluctuates abruptly, but does not exceed 7, even when liquefaction begins. Stability, budding power, raising time, and dead cells increase during keeping, all changes being hastened by increase in temperature. The following approximate times of storage at different temperatures, without significant change except in budding power, are given: 0° C. 2 to 3 months, 13 to 14° C. 2 weeks, 22 to 23° C. 1 week.

Nutritive Value of Yeasts.—Compressed yeast is especially rich in proteins, vitamins, enzymes, and phosphates. It contains as much protein as some cuts of meat and nearly twice as much as bread, although only about one-sixth as much carbohydrates and one-third as much fat as bread. Aside from its therapeutic value, it is a nutritious, easily digested food. The taste for raw yeast, if not natural, is soon acquired as witnessed by the great number of people who eat several yeast cakes daily. Cooked yeast, as noted below, because of its agreeable animal flavor, merits special mention. Sociologically, yeast is remarkable because of its rapid production from sugar, ammonia salts, and mineral food; meat requires months or years for production, bread cereals months, vegetables weeks, but yeast only a few days.

Yeast as a Meat Substitute.—Among those who recommend yeast as a meat substitute are Salomon² and Walter.³ In addition to its high nitrogen content, the presence of purines contributes meatlike characteristics. The striking chemical difference between meat and yeast extract, as brought out by Micko, Volume III, p. 397, is that the chief purine of meat extract is *hypoxanthine*, whereas that of yeast extract is *adenine*; furthermore the former contains both *creatine* and *creatinine*, whereas the latter contains neither. In addition to adenine, yeast extract contains small amounts of *hypoxanthine*, *xanthine*, and *guanine*.

What is of more importance than these stimulating constituents is the flavor. Not only yeast extract, but cooked compressed yeast, has an animal flavor which strikingly resembles that of shellfish, notably clams and scallops. Balls of compressed yeast and potatoes fried like doughnuts are particularly acceptable. Salomon² recom-

¹ Przemysl Chem. 1934, **18**, 93.

² Münch. Med. Woch. 1916, **63**, 445.

³ Arch. ges. Physiol. 1920, **181**, 271.

mends the addition of yeast to potato soup. Dishes of this sort should prove a boon to those choosing or forced to restrict their diet to vegetable foods, who often confess to a longing for an animal flavor which it is hard to overcome.

Relation of Yeast to Mushrooms.—A close botanical and chemical relationship exists between yeast and mushrooms. The glycogen of yeast is represented by the trehalose of mushrooms; yeast cellulose is doubtless similar to, if not identical, with mushroom cellulose; the ash of both yeast and mushrooms, so far as results are available, consists chiefly of potash and phosphoric acid. Data are insufficient to warrant comparison of the proteins and their amino acids.

Whether the fact that both chlorophyll-free plants and animals derive their carbon only from ready-formed organic substances, not by photosynthesis, explains a certain similarity in composition of yeast and mushrooms with muscle and liver, or whether the constituents common to these hark back to a common ancestor in the early stages of life on the planet, is mere conjecture.

FERMENTATION.—The fantastic theories of fermentation antedating the discovery of oxygen and hydrogen have little interest for the scientist. Lavoisier¹ was the first to make a quantitative study of the reactions, the results of which led Gay-Lussac in 1810 to frame the equation discussed in a subsequent section. These early chemists had no intimation that the reactions were of biological origin, and even after Cagniard-Latour,² Schwann,³ and Kützing,⁴ working separately, submitted microscopic evidence that the living yeast plant brought about the changes, Berzelius, Wöhler, and Liebig ridiculed the biological theory.

Liebig remained a doubter when Pasteur's evidence had gained general credence elsewhere. One of us was privileged to hear from Samuel W. Johnson, under whom he studied and for many years labored, first-hand accounts of Liebig's lectures on fermentation. Pasteur's yeast plants were sarcastically referred to as bugs that ate sugar and excreted alcohol. As late as the early seventies Liebig still defended his theories.

Once having gained a foothold, for nearly a generation the biological theory held unchallenged sway until Buchner⁵ announced his dis-

¹ *Traité élémentaire de chimie*, 1789, Chap. XIII.

² *Ann. chim. phys.* 1838, **68**, 206.

³ *Ann. Physik* 1837, **41**, 184.

⁴ *J. prakt. Chem.* 1837, **11**, 385.

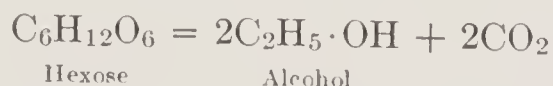
⁵ *Ber.* 1897, **30**, 117, 1110; 1898, **31**, 568.

covery, almost as revolutionary as Pasteur's, that fermentation may be induced in the absence of cells by means of yeast juice. He thus demonstrated that Liebig was only half wrong and Pasteur was only half right. The whole truth is in substance that yeast secretes the enzyme *zymase* which, both in the presence or the absence of the yeast cell, acts on the sugar molecule with generation of carbon dioxide and alcohol as the ultimate products.

Factors Influencing Fermentation.—Natural yeasts differ in the kinds and extent of the reactions they bring about, and these differences may be intensified by cultivation. Reactions are also influenced by the constituents, both organic and inorganic, of the fermenting medium in which the yeast is prepared and of the natural or added yeast foods present in the dough. Temperature, time, and aeration are important factors. Even when the strain of yeast is the best obtainable, the medium is of approved formula, and the conditions supposedly normal, continual vigilance is essential for success.

The tiny yeast cell, that shows its internal structure only with the higher powers of the microscope, is a laboratory in which are synthesized a surprisingly large number of organic and inorganic substances of known constitution, as well as enzymes of unknown constitution, but of known activity, ready to act when given the proper conditions. Yet out of this maze of potential reactions, known and unknown, Gay-Lussac's equation as given below stands supreme. The industry of yeast manufacture is carried out with remarkable precision when it is considered that it is the countless millions of dustlike cells that do the work, or rather elaborate the enzymes that do the work, the manufacturer's part being merely to supply the raw material and regulate the conditions.

Gay-Lussac's Theory.—The equation of Gay-Lussac,¹ based on the classical analyses of Lavoisier, although now known to represent only the beginning and end of more complicated changes of anaerobic fermentation, has lost nothing in practical value with time, since the reaction is roughly quantitative:



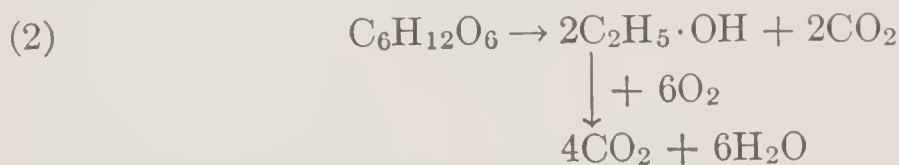
It is this reaction that is fundamental for the liquor industry because of the high yield of alcohol. It also applies to bread making.

As stated by Frey, Kirby, and Schultz,² when only the end prod-

¹ Extract d'un mémoire sur la fermentation, Ann. chim. phys. 1810, 76, 245.

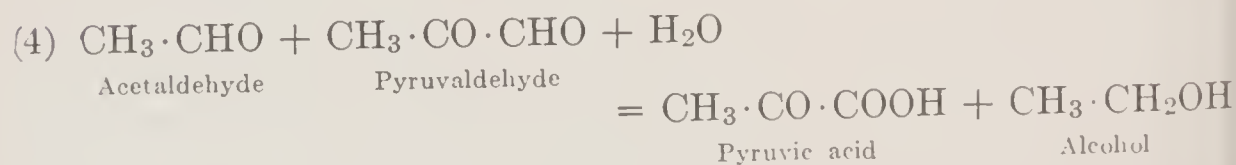
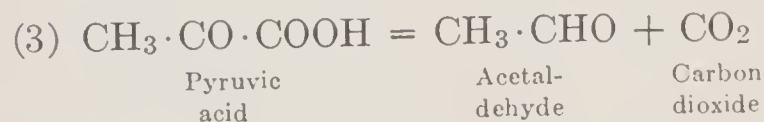
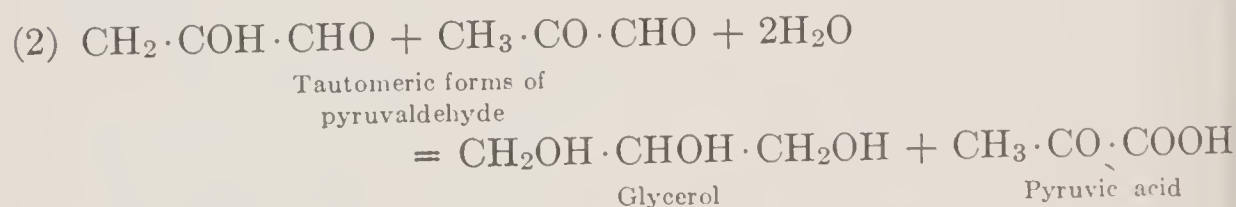
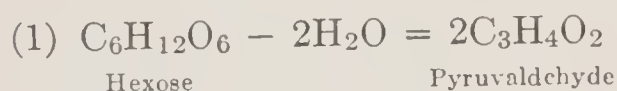
² Ind. Eng. Chem. 1936, 28, 879.

ucts CO_2 and H_2O are considered, aerobic fermentation (respiration) with complete oxidation may take place according to one of two possible reactions:



As the volume of oxygen consumed is equal to that of the carbon dioxide formed, these reactions would not bring about raising in bread making; they are, however, important in the manufacture of yeast where it is high yield of yeast cells, not alcohol, and high utilization of sugar that is desired.

Neuberg's Pyruvic Acid Theory.—Neuberg and Kerb¹ developed a purely organic theory of fermentation, based on the results of numerous experiments, which has been widely accepted, at least for the final (phosphorus-free) stages. The reactions are as follows:



The first of the reactions is probably the resultant of two or three stages; the second and fourth are Cannizzaro reactions, an acid and an alcohol being formed from two and one aldehydes respectively.

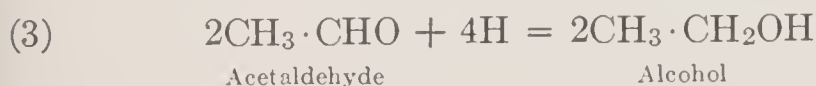
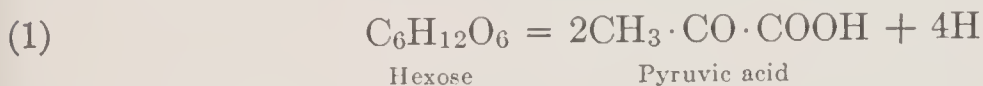
Harden,² after an exhaustive analysis of the extensive data, concludes that a considerable part of Neuberg's theory has been confirmed. The most important proofs were (1) the presence of a substance reducible to glycerol, (2) the formation of acetaldehyde from

¹ Biochem. Z. 1912, **43**, 494; **47**, 405, 413; 1913, **53**, 158.

² Alcoholic Fermentation, London, 4th Ed. 1932, p. 135.

pyruvic acid by carboxylase, and (3) the reduction of acetaldehyde to alcohol.

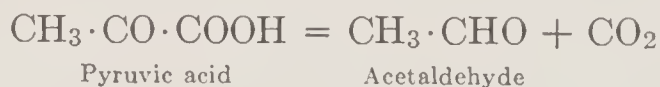
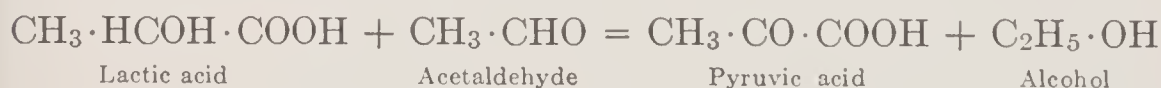
Kostytschev's Pyruvic Acid Theory.—Kostytschev and associates¹ advance a quite simple theory involving only *pyruvic acid* and *acetaldehyde* as transition products between hexose and alcohol, as illustrated by the three following reactions:



In support of this theory is the power of *carboxylase* to convert pyruvic acid into acetaldehyde and carbon dioxide and of other yeast enzymes to reduce acetaldehyde to alcohol.

Schade's Formic Acid Theory.²—This depends on (1) action of alkali on a hexose with formation of *lactic acid*, (2) splitting of lactic acid into *acetaldehyde* and *formic acid*, and (3) reduction of acetaldehyde to *alcohol* with evolution of *carbon dioxide*. The theory and suggested modifications, although consistent with certain experimental data, appear to have few supporters.

Palladin and Sabinin's Lactic Acid Theory.—The following reactions are given by Palladin and Sabinin³ whereby *pyruvic acid* and *alcohol* are formed from *lactic acid* and *acetaldehyde* in dead cells and the pyruvic acid is then split into carbon dioxide and acetaldehyde:



All lactic acid theories are regarded as obsolete.

Harden and Young's Hexose Diphosphate Theory.—A new epoch in fermentation chemistry began in 1905 when Harden and Young⁴ demonstrated that addition of phosphate to a fermenting dextrose and

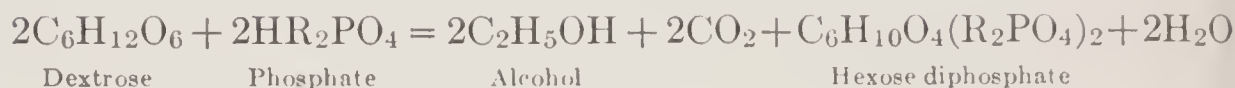
¹ Z. physiol. Chem. 1912, **79**, 130, 359; 1913, **83**, 93; Ber. 1913, **46**, 339; Kostytschev and Hübbenet: Z. physiol. Chem. 1913, **85**, 408.

² Z. physik. Chem. 1906, **57**, 1.

³ Bul. acad. sci. Petrograd 1916, p. 187.

⁴ Roy. Soc. London 1905, (B), **77**, 405; 1906, **78**, 369; 1908, **80**, 296; Proc. Chem. Soc. 1908, **24**, 115.

yeast juice solution causes (1) the formation of *hexose diphosphate* which is not precipitated by magnesium mixture, (2) accelerates the fermentation, and (3) increases the *carbon dioxide* and *alcohol* formed in proportion to the phosphate added, thus:



Hydrolysis of the hexose phosphate resulted in the regeneration of the hexose and the phosphate.

The discovery of *hexose diphosphate* ("Harden and Young ester") and of *hexose monophosphate* ("Robison ester") has been of fundamental value in elucidating the preliminary stages of fermentation. The phosphorus content of yeast juice, however, is no index of fermentative power, since, as shown by Buchner and Haehn,¹ in certain forms the phosphorus is inactive.

Maclea and Hoffert² report results in support of the view that the component molecules dextrose and phosphate of the hexose phosphate molecules pass through the walls of the yeast cells and there combine, but the hexose phosphate thus formed cannot pass through the walls. Lang and Nielsen³ corroborate this view, adding that the walls are impermeable to adenyolphosphoric acid as well as hexose phosphate.

Kluyver and Struyk⁴ discuss the stages of yeast fermentation. Addition of disodium and monosodium phosphates increased fermentation, but in different rates and degrees according to the type of yeast. With some yeasts, especially when the separation was by Robison's method, 45 per cent of the phosphate consisted of *hexose diphosphate*; with other types only a trace was in this form. The formation of *triose phosphate* also varied with the type.

Nilsson and Alm,⁵ starting with the thesis that *hexose monophosphate*, an intermediate product of fermentation, splits by an intramolecular oxidation-reduction process into *glycerophosphate* and a *triose*, postulate that by varying the proportion of sugar to phosphoric acid (3:2 and 2:1) the proportion of the products, including fermentable and unfermentable triose, is changed. As evidence that phos-

¹ Biochem. Z. 1910, **27**, 418.

² Biochem. J. 1924, **18**, 1273.

³ Nature 1937, **140**, 725.

⁴ Verslag. Akad. Wetenschappen Amsterdam 1927, **36**, 608.

⁵ Biochem. Z. 1936, **286**, 254.

phorylation plays a part in fermentation, McFarlane¹ cites the decrease in *orthophosphate* in the yeast at the start and the return to the original amount at the end. About 30 per cent of the phosphorus of yeast was found to exist as an *iron, nucleic acid, and metaphosphoric acid* complex.

Lebedev's Hexose Diphosphate Theories.—Lebedev in about four years proposed three theories involving hexose diphosphate and triose monophosphate.

In the first theory,² hexose is split into *dihydroxyacetone* and *glyceraldehyde*; then *triose monophosphate* is formed from dihydroxyacetone and passes into *hexose diphosphate*. The latter reacts with one molecule of water to form *alcohol, carbon dioxide, triose monophosphate*, and the original phosphate.

The second theory³ postulates two series, the first involving the reactions of the first theory up to the formation of *hexose diphosphate*, one molecule of which reacts with two of water reforming hexose and the original phosphate. The second series starts with *glyceraldehyde*, which splits into *glycerol* and *glyceric acid*. The latter is converted into *pyruvic acid*, which is acted on by *glyoxalase* and passes through the stages given under Kostytschev's theory.

In the third theory,⁴ *glyceraldehyde* oxidizes to *glyceric acid*, which, by withdrawal of one molecule of water, is changed into *pyruvic acid*. Four molecules of *pyruvic acid*, by hydrolysis, pass into two molecules each of *alcohol* and *acetaldehyde*, four molecules of *carbon dioxide*, and one of *oxygen*, the latter balancing the *oxygen* required for the initial formation of *glyceric acid*, analogous to the liberation and utilization of *hydrogen* in Kostytschev's theory.

Although partly based on sound evidence, the theories may be regarded as ingenious studies in equations involving the principal substances identified in fermenting liquids.

Meyerhof's Hexose Diphosphate-Pyruvic Acid Theory.—Meyerhof and Kiessling⁵ confirmed the theory of Embden, Deuticke, and Kraft⁶ for the process of glucolysis in muscle. They obtained a yield of 70 per cent formed from α -phosphoglycerol which also was isolated. Up to the *pyruvic acid stage*, they considered that yeast fermentation fol-

¹ Biochem. J. 1936, **30**, 1369.

² Compt. rend. 1911, **153**, 136.

³ Biochem. Z. 1912, **46**, 483; Ber. 1912, **45**, 3256.

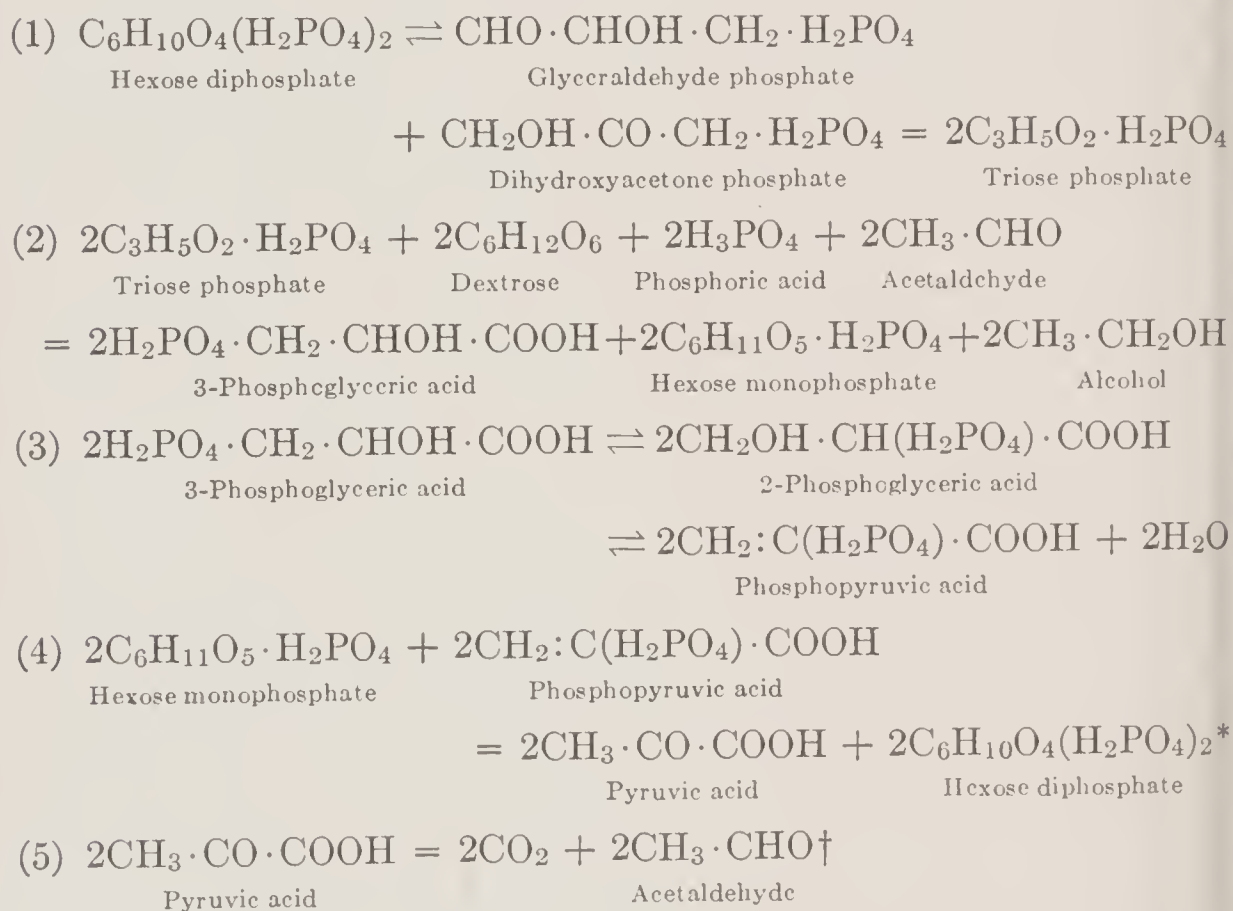
⁴ Ber. 1914, **47**, 660.

⁵ Naturwissensch. 1933, **21**, 223; Biochem. Z. 1933, **264**, 40; 1934, **267**, 313; 1935, **281**, 249; **283**, 83.

⁶ Klin. Wochschr. 1933, **12**, 213.

lows the same course as in muscle metabolism, but that thereafter pyruvic acid, instead of reacting with α -phosphoglycerol to form *lactic acid* and *triose monophosphate* as in muscle, splits up in the presence of phosphoric acid, dextrose, and yeast with formation of *carbon dioxide*, *alcohol*, and *3-phosphoglyceric acid* as end products.

The series of reactions as first formulated was revised by Meyerhof and Christian¹ and again by Meyerhof, Kiessling, and Schultz² as shown below. The authors state that fermentation involves reversible and irreversible reactions, phosphorylation and dephosphorylation, in conjunction with the functioning of an adenylic acid system, hydrogenation, and the action of cozymase. Nearly every step in the series is based on experimental evidence.



* Reenters equation (1). † Reenters equation (2).

Kobel and Neuberg³ demonstrated the presence of free trioses by distillation with sulphuric acid which converts the trioses almost quantitatively into pyruvaldehyde, $\text{CH}_3 \cdot \text{CO} \cdot \text{CHO}$.

The question naturally arises how is Myerhof's theory, involving the various phosphoric acid compounds, which may be regarded as an

¹ Biochem. Z. 1936, 286, 281.

² Ibid. 1937, 292, 25.

³ Ibid. 1934, 269, 441.

amplification of the Harden and Young reaction, to be reconciled with the phosphorus-free theory of Neuberg which, in its final form, Harden regards as logical in practically every step. When the whole truth is known and due consideration is given to enzymic action, the variation in yeast and mediums, and other variable conditions of fermentation, it is not unreasonable to expect that the two theories will have much more in common than now appears on the surface. Harden voices the belief, shared by others, that it is in the early stages of fermentation that phosphate is essential.

MICROSCOPIC STRUCTURE (Fig. 134). **Cell Forms.**—The yeast *Saccharomyces cerevisiæ* Meyen is a unicellular fungus, oval in shape, about 8 to 10 μ long and 7 to 9 μ in diameter. Under normal condi-

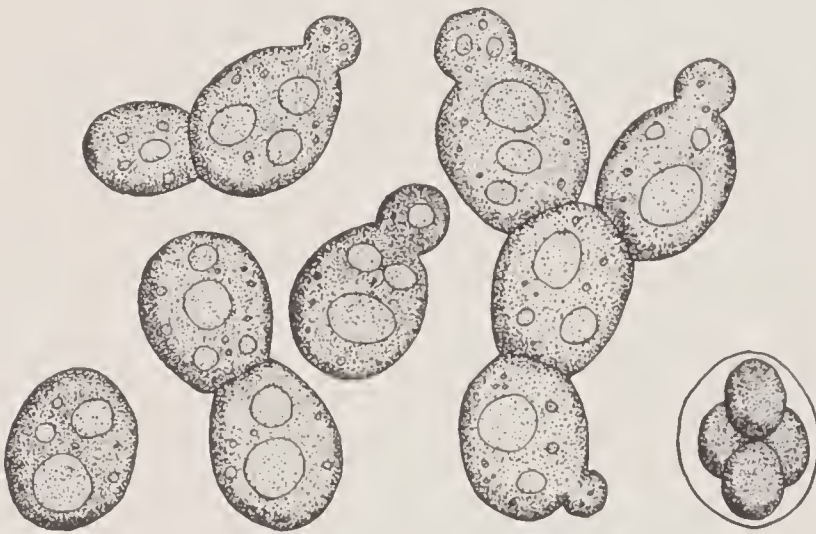


FIG. 134.—Yeast. At left, single cell; at right, resting cell with spores; in center, budding cells. $\times 1500$. (K.B.W.)

tions, the active plant consists of a single cell with a delicate wall and finely granular contents in which are embedded a nucleus, fat globules, and one or more vacuoles. These cells multiply by “budding,” the new cells breaking off as individuals or remaining loosely attached in chains or treelike aggregates. After the nutrient substratum has been exhausted, the yeast, with suitable temperature and access to oxygen, may go into a “resting stage” with slight increase in size and separation of the cell contents into spores.

Schumacher¹ classifies the parts of the yeast cell as (1) *Gram-positive endoplasm* containing lipoid; (2) *Gram-negative cell membrane* consisting of a phosphoglycoprotein containing sulphur, iron, and glucosamine, but no lipoid or lipoid complex, although the mem-

¹ Centr. Bakt. Parasitenk. 1928, I Abt. Orig. 108, 193.

brane of the spore wall does contain a lipoid-protein complex; and (3) weakly *Gram-positive cementing matter* containing a nitrogenous phospholipoid soluble in hot alcohol.

Sexual yeasts, as noted by Satava,¹ have markedly lower fermenting power than *asexual* or ordinary budding forms, owing to lower contents of certain enzymes.

Jonás² finds evidence that yeasts continue their existence not only by means of budding and sporulation but also by the hitherto undescribed *plasomes*. These latter are corpuscles 0.2 to 0.8 μ in diameter, without confining membranes, obtained from the amorphous plasma of pure cultures of yeast cells killed by chemical or physical means. The plasomes eventually give rise to definite cell forms.

Mary Holt³ traces the cause of the formation of *giant cells* to four amino acids, namely aspartic acid, glutamic acid, glycine, and alanine. They begin to form after 2 to 4 days. As high as 60 per cent yield of giant cells was obtained in 6 days with aspartic acid. Other yeast constituents are without effect.

Euler⁴ describes, in addition to dead and living yeast cells, *zy-matic cells* which, although not dead, are unable to reproduce.

Staining.—Dead yeast cells take up suitable stains and in this way can be readily distinguished from the live ones which remain colorless.

Hachn and Glaubitz⁵ state that the *methylene blue test* for dead cells is reliable only when the staining is distinct. Counting should be made immediately. This is corroborated by Fuchs.⁶ As pointed out by Fink and Weinfurtner,⁷ the reaction of the medium influences greatly the staining. Fink and Kühles⁸ prepare the staining solution by mixing equal volumes of methylene blue solution (1:10,000) and a phosphate buffer containing 1 part of 0.2 *M* disodium hydrogen phosphate to 399 parts of 0.2 *M* monosodium dihydrogen phosphate.

Brandrup⁹ endorses Grüber's *neutral red dye* (0.1:50) as a stain.

Staiger and Glaubitz¹⁰ voice a common protest against ignoring organoleptic evidence. Estimation of dead cells and leavening power should be supplemented by appearance and smell.

CHEMICAL COMPOSITION.—The composition of yeast, compared with that of common vegetable foods, is remarkable for the high con-

¹ Bul. assoc. élèves inst. sup. fermentations Gand 1934, **35**, 278.

² Biochem. Z. 1931, **239**, 140.

³ Trans. Roy. Soc. Can. 1928, [3], **22**, III, 269.

⁴ Z. Gärungsphysiol. 1914, **5**, 1.

⁵ Wochschr. Brau. 1929, **46**, 315.

⁶ Ibid. p. 437.

⁷ Ibid. 1930, **47**, 89, 110, 124.

⁸ Z. physiol. Chem. 1933, **218**, 65.

⁹ Apoth. Ztg. 1930, **45**, 522.

¹⁰ Brenneri-Ztg. 1931, **49**, 112.

tents of protein ($N \times 6.25$) and glycogen and the low content of fat. Oil seeds have high protein content, but associated with it is high fat content. Glycogen does not occur in ordinary vegetable foods. These points are brought out in the following analyses of compressed yeast by Frey: ¹

COMPOSITION OF COMPRESSED YEAST (FREY)

	Water	Protein	Fat (ether extract)	Glycogen	Cellulose, gum, etc.	Ash
	%	%	%	%	%	%
As sold	73.00	14.15	0.46	8.16	1.87	2.36
Dry substance	52.41	1.72	30.25	6.88	8.74

Influence of Yeast on Bread.—Pajetta ² made comparative analyses of leaven and compressed yeast bread, also of the flour, with the following results on the dry basis:

	Flour	Crust		Crumb	
		Leaven	Yeast	Leaven	Yeast
	%	%	%	%	%
Nitrogen	2.18	2.25	2.25	2.25	2.25
Sugar (as maltose)	1.57	1.97	2.26	2.25	5.77
Dextrin	1.60	0.78	0.61	0.23	0.77
Acid as lactic	0.21	0.43	0.17	0.72	0.30

CONSTITUENTS OF YEAST AND FERMENTING MEDIUMS.

Proteins.—Adolph Meyer, the distinguished agricultural chemist and fermentologist, as noted by Donath, ³ appears to deserve the credit for proving that yeast protein may be synthesized from purely inorganic constituents.

Our knowledge of the two proteins cerevisin and zymocasein is largely due to the papers published by Thomas and co-workers ⁴ before and after the World War, with some repetition, as summarized below:

¹ Ind. Eng. Chem. 1930, **22**, 1154.

² Atti I° cong. intern. panificazione Roma 1932, p. 45.

³ Oesterr. Chem. Ztg. 1915, **18**, 74.

⁴ Thomas and Kolodsiejska: Compt. rend. 1913, **157**, 243; Thomas: Bul. soc. chim. biol. 1919, **1**, 67; Thomas and Chabas: Compt. rend. 1920, **170**, 1622; Thomas: Ann. inst. Pasteur 1921, **35**, 43.

Cerevisin, an albumin, contained 16.25 per cent of nitrogen and 0.9 per cent of sulphur. It was soluble in water, coagulating between 41 and 70° C. Thomas¹ attributes to *cerevisin* an amylolytic power similar to that of sucrase.

Zymocasein, a phosphoprotein, contained 16.15 per cent of nitrogen and 1.8 per cent of sulphur. It was insoluble in water, but soluble in dilute alkali and coagulated with rennet.

Fungus Mucin.—Meigen and Spreng² prepared the vegetable glycoprotein fungus mucin of Nägeli and Loew by boiling dry defatted yeast with water, removing substances precipitated by lead acetate, deleading the solution, precipitating several times with alcohol, and drying with alcohol and ether. It polarizes +58.5° in water and on hydrolysis yields mannose and dextrose.

Amino Acids of Yeast Proteins.—The following results were obtained by the Abderhalden and Fuchs method:

PRODUCTS OF HYDROLYSIS OF YEAST PROTEINS (THOMAS)

	Cerevisin	Zymocasein
	%	%
Aspartic acid	1.00*	1.00*
Glutamic acid	6.26	0.84
Tyrosine	4.13	2.85
Tryptophane	2.28	1.51
Arginine	4.42	3.58
Lysine	8.10	4.09
Histidine	2.02	2.63

* Approximate.

Attention is directed to the high percentages of tryptophane and lysine in the above table.

Meisenheimer³ identified by Fischer's ester method the following monoamino acids produced by autolysis of yeast, in the presence of toluene: *glycocoll*, *alanine*, *valine*, *leucine*, *aspartic acid*, *glutamic acid*, *tyrosine*, *phenylalanine*, *proline*, and *tryptophane*. There was uncertainty as to the presence of *serine* and *cystine* but *amino butyric acid* appeared to be present, as was also, in the cell residue, *glucosamine*. In a later paper,⁴ he included diamino acids, ammonia, and purine and

¹ Compt. rend. 1914, 158, 1597.

² Z. physiol. Chem. 1908, 55, 48.

³ Wochschr. Brau. 1915, 32, 325; Z. physiol. Chem. 1919, 104, 229.

⁴ Z. physiol. Chem. 1921, 114, 205.

pyrimidine bases. His quantitative results appear below under Nitrogen Distribution in Yeast Proteins. Although given in terms of nitrogen in the different forms, the figures on amino acid nitrogen roughly represent the percentages in the protein ($N \times 6.25$), since they do not vary greatly in nitrogen content.

Csonka¹ obtained the following results on (1) water-soluble protein (albumin) obtained by heat coagulation, (2) salt-soluble protein (globulin) obtained by heat coagulation and by acid precipitation, and (3) alkali-soluble protein.

PRODUCTS OF HYDROLYSIS OF WATER- AND ASH-FREE YEAST PROTEINS (CSONKA)

	Water-soluble	Salt-soluble		Alkali-soluble
		Heat coagulation	Acid precipitation	
	%	%	%	%
Baker's yeast:				
Cystine	0.44	0.82	0.87	0.69
Tyrosine	4.79	3.96	4.44	3.11
Tryptophane	2.66	3.18	2.96	1.79
Brewer's yeast:				
Cystine	0.49	0.61	0.31
Tyrosine	4.11	3.85	3.93
Tryptophane	2.67	2.49	1.68
Arginine	3.50	2.82
Lysine	4.50	4.53
Histidine	1.38	tr.

Block² reviews the literature on the nature and origin of yeast proteins.

Abderhalden and Bahn³ demonstrated that edestin and yeast proteins contain *l*(+)- α -aminobutyric acid. Yeast proteins also yield *l*(+)-norvaline, *l*(+)-norleucine, and *l*(+)-isoleucine, and evidently hydroxyamino acids.

Nelson, Heller, and Fulmer⁴ regard yeast proteins as containing all the amino acids essential for growth. Kraut and Schlottmann⁵ found that they are intermediate between plant and animal proteins, the high cystine and lysine content being of special interest.

Maceration juice obtained from dried yeast by Lebedev's method,

¹ J. Biol. Chem. 1935, 109, 703.

³ Z. physiol Chem. 1937, 245, 246.

² Yale J. Biol. Med. 1935, 7, 235.

⁴ J. Biol. Chem. 1923, 57, 415.

⁵ Biochem. Z. 1937, 291, 406.

according to Neuberg,¹ yielded yeast protein, by coagulation, precipitation, filtering, washing, dehydrating with absolute alcohol, and grinding with alcohol and ether. One preparation contained nitrogen 13.15, sulphur 0.93, and phosphorus 0.61 per cent; others were of similar composition. Hydrolysis and isolation of the amino acids by Fischer's method gave the usual amino acids including tryptophane (0.2 per cent).

Nitrogen Distribution in Yeast Proteins.—Thomas and Kolodziej-ska's results on cerevisin and zymocasein follow: human nitrogen 1.69 and 4.02, basic nitrogen 23.69 and 26.67, monoamino nitrogen 67.03 and 60.39, and ammonia nitrogen 5.89 and 6.86 per cent respectively.

Meisenheimer² gives approximate figures on the percentages of nitrogen as mono- and diamino acids, ammonia, purine and pyrimidine bases, choline, and glycosamine in the total nitrogen after hydrolysis as follows:

NITROGEN DISTRIBUTION IN YEAST PROTEIN (MEISENHEIMER)

	%
Monoamino acids.....	58.50
Glycocoll.....	5.0
Alanine.....	10.0
Valine.....	10.0
Leucine.....	5.0
Cystine and other sulphur compounds..	2.0
Aspartic acid.....	3.5
Glutamic acid.....	6.0
Tyrosine.....	2.0
Phenylalanine.....	8.0
Proline.....	2.0
Oxyproline.....	4.5
Tryptophane.....	0.5
Diamino acids.....	20.00
Histidine.....	5.0
Arginine.....	5.0
Lysine.....	10.0
Ammonia.....	8.00
Purine and pyrimidine bases.....	12.00
Guanine.....	4.0
Adenine.....	4.0
Cytosine and uracil.....	4.0
Choline.....	0.50
Glycosamine.....	0.50
	<hr/>
	99.50

¹ Wochschr. Brau. 1915, **32**, 317.

² Z. physiol. Chem. 1919, **104**, 229; 1921, **114**, 205.

Yeast albumin, as hydrolyzed by Kiesel,¹ yielded as follows: humin nitrogen 15.22, ammonia nitrogen 4.50, histidine nitrogen 5.22, arginine nitrogen 7.96, and lysine nitrogen 7.96 per cent.

Free Amino Acids.—Ehrlich and Wendell² devised a method, employing yeast, for converting racemic amino acids into their active forms. From this it would appear that only active amino acids occur in yeast, but further data are not available.

Amines.—See also table above.

Many yeasts are stated by Ehrlich and Pistschimuka³ to attack primary amines with elimination of ammonia and formation of alcohol, the amines being regarded as intermediate products between amino acids and alcohol.

Of the amines formed from ammonia during antiseptic autolysis of yeast, Ivanov⁴ identified *amylamine*, or its iso form, and *trimethylamine*.

Purine Bases.—See also table above.

Kuen and Püringer⁵ found in fresh and dry yeast 1.06 per cent of *purine nitrogen*, dry basis, equivalent to 13.08 per cent of the total nitrogen.

Xymin, the *purine hexoside* of Mandel and Dunham,⁶ according to Levenne,⁷ contains a peculiar sugar that appears to be a *ketohexose*, but not a common 2-ketohexose.

Pyrimidine Bases.—See also table above.

Choline Bases.—See also table above.

Choline, $(\text{CH}_3)_3 : \text{N}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CH}_2\text{OH}$.—By fractioning the hot water extract of fresh brewer's yeast, Vickery⁸ obtained choline corresponding to 2.07 per cent of the nitrogen in the original extract. Betaine type bases were not found.

Chitin.—Although vegetable chitin has been reported in the cell walls of various lower organisms, Schmidt⁹ was unable to isolate it from budding yeasts.

Hydrocyanic Acid.—Pourbaix and Kenneway¹⁰ believe that several factors are responsible for the nitroprusside reaction of yeast.

Fat.—Maclean¹¹ concluded that normally yeast contains little free fat, the greater part being combined with protein and perhaps carbohydrate and not being directly extractable by alcohol and ether.

¹ Ibid. 1922, 118, 304.

² Biochem. Z. 1908, 8, 438.

³ Ber. 1912, 45, 1006.

⁴ Biochem. Z. 1914, 58, 217.

⁵ Ibid. 1934, 272, 113.

⁶ J. Biol. Chem. 1912, 11, 85.

⁷ Ibid. 1924, 59, 465.

⁸ Ibid. 1926, 68, 585.

⁹ Arch. Mikrobiol. 1936, 7, 241.

¹⁰ Biochem. J. 1928, 22, 1112.

¹¹ Ibid. 1922, 16, 370.

Lindner¹ followed the progressive formation of fat by yeast cells by microscopic examination coupled with color reactions, thus immediately reaching conclusions which, depending on fermentation experiments and fat determinations by chemical methods, would have required days of study.

Macleane and Hoffert² theorize that carbohydrate storage is either in the form of glycogen or a related substance hydrolyzing to reducing sugar, or else in the form of a hexose phosphate representing the first stage in changing from carbohydrate to fat.

Daubney and Smedley-Macleane³ recognized that the fortification of sugar solutions with phosphate increases the content of fat, phospholipides (phospholipins), and sterols in the yeast.

By reducing the water content of bottom brewer's yeast by alcohol vapor and aeration, Sobotka, Halden, and Bilger⁴ increased the fat and sterol contents. There was no correlation between the fat and nitrogen contents, but Halden⁵ found that the ratio of sterols to fat increased from 0.111 to 0.312.

Composition.—Neville⁶ concludes that the chief saturated acid of yeast fat is one with 15 carbon atoms and that *arachidic acid* is present in small amount. Of the unsaturated acids, the presence of three with 16 and 30, 18 and 32, and 18 and 34 carbon and oxygen atoms respectively was demonstrated. Maclean and Thomas⁷ identified *palmitic*, *oleic*, and *linolic acids*; *lauric* and *arachidic* were also probably present. Ergosterol formed about 20 per cent of the fat.

In yeast fat, amounting to 2 per cent of the dry and 0.5 per cent of the compressed product, Weichherz and Merländer⁸ established the presence of *valeric acid* and produced evidence of the probable presence of *caproic acid*. Higher non-volatile acids are also believed to be present.

Newman and Anderson,⁹ with alcohol and ether, extracted "lipides" similar to the fat of animals and plants, equivalent to 6.02 per cent of the dried yeast. With alcohol containing 1 per cent of hydrochloric acid, 0.86 per cent additional was extracted. By saponification of the

¹ Z. angew. Chem. 1922, **35**, 110.

² Biochem. J. 1923, **17**, 720.

³ Ibid. 1927, **21**, 373.

⁴ Z. physiol. Chem. 1935, **234**, 1.

⁵ Fettchem. Umschau 1935, **42**, 29.

⁶ Biochem. J. 1913, **7**, 341.

⁷ Ibid. 1920, **14**, 483.

⁸ Biochem. Z. 1931, **239**, 21.

⁹ J. Biol. Chem. 1933, **102**, 219.

acetone-soluble portion (fat), they obtained glycerol, fatty acids, and sterols, also cyclic and bicyclic hydrocarbons ranging from $C_{19}H_{38}$ to $C_{34}H_{66}$ due to impurities in the yeast. The saturated acids consisted essentially of *palmitic* 75 per cent and *stearic* 25 per cent, together with a trace of an acid lower than palmitic; the unsaturated acids, constituting 60 per cent of the total acids, on reduction, yielded 25 per cent of palmitic and 75 per cent of stearic acids.

The following figures were obtained by Täufel, Thaler, and Schreyegg¹ on yeast fat:

	%
Volatile acids.....	5.2
Stearic acid.....	5.9
Palmitic acid.....	9.5
Oleic acid.....	47.6
Linolic acid.....	2.9
Glycerol.....	5.3
Unsaponifiable matter	
Ergosterol {	
Cryptosterol }	3.3
Squalene (I No. 371.1)	16.3
	<hr/>
	19.6
	<hr/>
	96.0

Sterols. *Ergosterol*, $C_{27}H_{42}O$.—Windaus and Grosskopf² announced in 1922 that *ergosterol*, previously found by Tanret in ergot, occurs also in yeast fat. It may be prepared from yeast by their method as simplified by Heiduschka and Lindner.³ Ergosterol of yeast fat was crystallized by Reindel, Walter, and Rauch⁴ from alcohol with one molecule of water and from ether in anhydrous form with a melting point 160 to 161° C. and a specific rotation of -117° , changed later to -130° . Reindel and Walter⁵ and Reindel and Detzel⁶ studied the derivatives.

Earlier statements by Daubney and Smedley-Maclean⁷ that the unsaponifiable matter consists partly of sterol and partly of a saturated compound was modified by the authors⁸ after examination of additional samples.

¹ Z. Unters. Lebensm. 1936, 72, 394.

² Z. physiol. Chem. 1922, 124, 8.

³ Ibid. 1929, 181, 15.

⁴ Ann. 1927, 452, 34.

⁵ Ann. 1928, 460, 212.

⁶ Ibid. 1929, 475, 78.

⁷ Biochem. J. 1927, 21, 373.

⁸ Ibid., p. 869.

Of all the oils and fats examined spectroscopically by Heilbron, Kamm, and Morton,¹ that of yeast showed the strongest ergosterol bands.

The results of Bills, Massengale, and Prickett² show that the ergosterol content varies with the strain of yeast and the cultural conditions. They concluded that it is produced primarily by carbohydrate metabolism.

Determinations in dry yeast made by Castille and Ruppel³ show 0.1 to 0.7 per cent of ergosterol. Täufel, Thaler, and Schreyegg⁴ found 19.6 per cent of unsaponifiable matter in brewers' yeast fat and in the unsaponifiable matter 16.8 per cent of crystalline sterols, equivalent to 3.3 per cent of the fat, in which ergosterol and *cryptosterol* were identified. *Squalene*, equivalent to 16 per cent of the fat, was obtained from the residual liquid as a bright yellow oil.

By irradiation of baker's yeast, Matzko⁵ greatly increased the content of vitamin D. No loss was sustained during 2 months, but after 4 months a marked loss was observed. Others, however, find no loss after 10 months.

Zymosterol.—Smedley-Maclean⁶ isolated zymosterol ($C_{27}H_{42}O$) melting at 108 to 109° C. and with plus rotation. Penau and Tanret⁷ isolated from fresh yeast 0.1 per cent melting at 100 to 101° C. and with a specific rotation of +34° at 16° C. They proposed the formula $C_{27}H_{42}O_2 \cdot H_2O$, which has one more oxygen than Maclean's formula.

Reindel and Weickmann⁸ purified zymosterol by repeated crystallization from methyl alcohol, the final product showing melting point 107 to 110° C. (cor.) and specific rotation +49.2°. From crude zymosterol acetate, they prepared free zymosterol melting at 107 to 110° C. with a specific rotation +52.2°.

Miscellaneous Sterols.—The values of 3 yeast sterols isolated by Wieland and Asano,⁹ namely *fecosterol* ($C_{27}H_{46}O$), *ascosterol* ($C_{27}H_{46}O$), and *neosterol* ($C_{27}H_{44}O$), follow: melting point 161 to 163°, 141 to 142°, and 164 to 165° C.; specific rotation 42.1° at 25° C..

¹ Ibid., p. 1279.

² J. Biol. Chem. 1930, **87**, 259; 1931, **94**, 213.

³ Bul. acad. roy. méd. Belg. 1933, **13**, 48.

⁴ Loc. cit.; Fettechem. Umschau 1936, **43**, 26.

⁵ Arch. Tierernähr. Tierzucht 1933, **9**, 623.

⁶ Biochem. J. 1928, **22**, 22.

⁷ Bul. soc. chim. biol. 1928, **11**, 929.

⁸ Ann. 1929, **475**, 86; 1930, **482**, 120.

⁹ Ibid. 1929, **473**, 300.

45.0° at 20° C., and 105.0° at 24° C. Wieland and Gough¹ add the following: *episterol* ($C_{27}H_{44}O$), *anasterol*, *hyposterol*, and an *unnamed sterol* from the mother liquor of which *hyposterol* separated. The physical constants of these in the order named were: melting point 135 to 136°, 157 to 159°, 100 to 102°, and 144 to 146° C., specific rotation 6.2° at 20° C., -8.1° at 25° C., 12.5° at 20° C., and -33.8° at 25° C. Solubilities in chloroform and adsorption spectra are also given. Wieland and Stanley² isolated *cryptosterol* as benzoate, also in the same and other fractions what were probably *ergosterol* and α -*dihydroergosterol*.

According to Callow,³ α -*dihydroergosterol* occurs as an impurity in yeast *ergosterol*. *Cerevisterol*, accompanying *ergosterol* in yeast, has been isolated by Honeywell and Bills,⁴ who state that it has no anti-rachitic value.

Acids.—Neuberg and Tir⁵ list common organic acids and other substances that yield carbon dioxide by the action of yeast. Among the products of the alcoholic fermentation of tartaric acid by yeast, Karczag⁶ names *propionic*, *butyric*, *lactic*, and *acetic* acids.

Formic Acid.—See also Schade's theory of fermentation.

Formic acid occurs in small amount in fermenting liquids and may be present in minute amount in yeast.

Acetic Acid.—See also above.

Souring in access to air follows closely on the heels of alcoholic fermentation. No figures are available on the amount of acetic acid present in fresh or soured yeast.

Propionic Acid.—See above.

Pyruvic Acid (*Pyroracemic Acid*), enol form $CH_2 : COH \cdot COOH$; keto form $CH_3 \cdot CO \cdot COOH$.—Formerly the name was spelled *pyrouvic*; the descriptive name is *acetylcarboxylic acid*. Pyruvic acid figures in the fermentation theories of Kostytschev, Neuberg and Kerb, Palladin and Sabinin, and Meyerhof, which see.

1. Occurrence.—Fernbach and Schoen⁷ identified calcium pyruvate and calcium lactate in yeast fermentation taking place in the presence of calcium carbonate. Mazé and Ruit,⁸ by growing lactose yeasts and

¹ Ibid. 1930, 482, 36.

² Ibid. 1931, 489, 31.

³ Biochem. J. 1931, 25, 87.

⁴ J. Biol. Chem. 1932, 99, 71.

⁵ Biochem. Z. 1911, 32, 323.

⁶ Ibid. 1912, 43, 44.

⁷ Compt. rend. 1913, 157, 1478; 1914, 158, 1719; 1920, 170, 764; Compt. rend. soc. biol. 1922, 86, 15; 1923, 89, 475.

⁸ Compt. rend. soc. biol. 1917, 80, 336.

wine yeasts in a medium containing calcium lactate and inorganic salts, secured a yield of pyruvic acid as high as 50 per cent of the lactic acid in a reversible reaction. Fermentation with compressed yeast, however, as shown by Kerb,¹ Kerb and Zeckendorf,² and Kostytshev and Frey,³ yields only acetic, malic, and succinic acids.

Von Grab,⁴ by the use of β -naphthylamine as "fixing agent," obtained pyruvic acid as an intermediate product in fermentation, and others, employing various other fixatives, report similar results, albeit subjected to criticism by Neuberg and Kobel,⁵ as well as others. Neuberg and Kobel,⁶ by adjusting the volume of the medium to the dry weight of dried yeast, was able to stop the fermentation of hexose diphosphate at the pyruvic acid stage. The same authors, in a medium containing dextrose, magnesium and sodium phosphates, and magnesia, secured a yield of both pyruvic acid and glycerol.

2. Decomposition.—Neuberg and Hildesheimer,⁷ Neuberg and Tir,⁸ and others demonstrated that pyruvic acid, being an α -ketonic acid, and its salts are decomposed by the carboxylase of yeast with formation of acetaldehyde and liberation of carbon dioxide in the absence of the coenzyme so essential in the action of zymase on hexose.

3. Fermentability.—There is abundant evidence of the fermentation of pyruvic acid. Nord⁹ is of the opinion that it is the enol form of pyruvic acid that is decomposed in fermentation. Neuberg and Rosenthal¹⁰ found that pyruvic acid fermented under conditions not suited for action on levulose. Euler and Löwenhamm¹¹ state that toluene and chloroform accelerate the fermentation of pyruvic acid by fresh yeast. This is not true of dried yeast, although drying alone does not materially check the action on pyruvic acid.

Contrary to the conclusions of Maurer,¹² Fromageot and Desnuelle¹³

¹ Ber. 1919, 52B, 1795.

² Biochem. Z. 1921, 122, 307.

³ Z. physiol. Chem. 1925, 146, 276.

⁴ Biochem. Z. 1921, 123, 69.

⁵ Ibid. 1927, 191, 472.

⁶ Ibid. 1930, 219, 490; 229, 255, 446.

⁷ Ibid. 1911, 31, 170.

⁸ Ibid. 1911, 32, 323.

⁹ Mechanism of Enzyme Action and Associated Cell Phenomena, London, 1929, p. 43.

¹⁰ Biochem. Z. 1914, 61, 171.

¹¹ Z. physiol. Chem. 1916, 97, 279.

¹² Biochem. Z. 1927, 189, 216.

¹³ Bul. soc. chim. biol. 1936, 18, 820.

found that neither *pyruvic acid oxime* nor *acrylic acid* is an intermediate product in the change of pyruvic acid to *alanine* by yeast.

4. Properties.—It is a yellowish liquid, with an odor like acetic acid, miscible with water, alcohol, and ether; specific gravity at 15° C. 1.27; boiling point 165° C.

Butyric Acid.—See also above.

Among the results on butyric acid in a variety of animal and vegetable foods, reported by Grossfeld and Battay,¹ is one showing 0.019 per cent in compressed yeast.

Succinic Acid, $\text{COOH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$.—This acid, a white crystalline solid melting at 183° C., is one of the by-products of fermentation. It is formed, as shown by Ehrlich,² from glutamic acid, analogously to the formation of isoamyl alcohol from leucine. Further details are given by Harden.³

Lactic Acid, $\text{C}_3\text{H}_6\text{O}_3 + \text{C}_3\text{H}_6\text{O}_3$.—See also Schade's and Palladin and Sabinin's Theories.

1. Occurrence.—The formation of lactic acid from carbohydrates, through the agency of bacteria, in the souring of milk and the fermentation of sauerkraut and ensilage has long been known, but it was not until the laws of stereochemistry had been elucidated that the three forms were differentiated.



d-Lactic acid



l-Lactic acid

The *d*-form occurs in muscle as a result of muscular effort; it is also formed by certain species of bacteria. The *l*-form is produced by *Bacillus acidi lacti*. The *dl*-form, or inactive form, consisting of equal molecules of *d*- and *l*-forms, is made commercially from acetaldehyde; it is this form that occurs in sour milk, sauerkraut, and ensilage, also presumably in yeast fermenting media. Whether the specific bacteria produce one form directly or destroy one form only in the inactive mixture is uncertain.

Oppenheimer⁴ showed that formation of lactic acid takes place in the fermentation of yeast maceration juice and increases with addition of sugar, glyceric aldehyde, or dioxyacetone. Lieben⁵ pointed

¹ Z. Unters. Lebensm. 1931, 61, 129.

² Biochem. Z. 1909, 18, 391.

³ Alcoholic Fermentation, London, 1932, p. 171.

⁴ Z. physiol. Chem. 1914, 89, 45, 63.

⁵ Oesterr. Chem. Ztg. 1922, 25, 87.

out the analogy of the formation of lactic acid from carbohydrates by yeast to that taking place in muscle. Hahn and Dürr¹ noted that the presence of oxygen inhibits the formation of lactic acid, which explains the marked increase *in vacuo*.

2. Properties.—Pure anhydrous lactic acid of all forms is a colorless crystalline solid, but since it melts at room temperature, it is commonly known as a viscous liquid (specific gravity at 15° C. 1.22; specific rotation *d* +3.5°, *l* −3.5°, *dl* 0°; boiling point at 12 mm. 120° C.). It is soluble in water, alcohol, and ether, but not in petroleum solvents, benzol, or carbon bisulphide.

Nicotinic Acid, $C_5H_4N \cdot COOH$.—See p. xxix.

Vickery,² by fractioning the hot water extract of fresh brewer's yeast, obtained nicotinic acid corresponding to 0.28 per cent of the nitrogen in the original extract.

Nucleic Acid.—See Phosphorus-Organic Compounds.

Alcohols. *Methyl Alcohol (Methanol)*, $CH_3 \cdot OH$.—Takahashi, Gunke, and Yamazaki³ state that all kinds of yeast form methyl alcohol in fermentation, glyocol increasing the action.

Ethyl Alcohol (Ethanol), $C_2H_5 \cdot OH$.—See Alcoholic Fermentation.

Yeast was shown by Foth⁴ to retain about the same amount of alcohol as is present in the medium. In compressed yeast it increases during keeping.

Butyl Alcohol (Butanol), $C_4H_9 \cdot OH$.—Although butyl alcohol is now produced commercially through the agency of microorganisms, it is not formed in ordinary fermentation except possibly under abnormal conditions.

Amyl Alcohol.—Fusel oil, a by-product of alcoholic fermentation, consists largely of two liquid alcohols with a sickening odor, *d*-amyl alcohol ($CH_3 \cdot CH(C_2H_5) \cdot CH_2 \cdot OH$) and isoamyl alcohol ($((CH_3)_2 \cdot CH \cdot CH_2 \cdot CH_2 \cdot OH)$), chiefly the latter. These are derived, respectively, as shown by Ehrlich,⁵ from isoleucine ($CH_3 \cdot CH(C_2H_5) \cdot CH(NH_2) \cdot COOH$) and leucine ($((CH_3)_2 \cdot CH \cdot CH_2 \cdot CH(NH_2) \cdot COOH$), which are products of the hydrolysis of proteins. Further details are given by Harden.⁶

¹ Z. Biol. 1934, **95**, 298.

² J. Biol. Chem. 1926, **68**, 585.

³ J. Am. Chem. Soc. 1917, **39**, 2723.

⁴ Jahrb. Ver. Spiritus-fabrikanten in Deutschland 1914, **14**, 33.

⁵ Ber. 1907, **40**, 1027.

⁶ Alcoholic Fermentation, London, 1932, p. 167.

Glycerol, $(\text{CH}_2\text{OH})_2 : \text{CHOH}$.—This alcohol, together with amyl alcohol and succinic acid (which see) form the three chief by-products of alcoholic fermentation.

Saligenin, $\text{C}_6\text{H}_4(\text{OH}) \cdot \text{CH}_2\text{OH}$.—Mayer ¹ found that saligenin was formed from salicylaldehyde by yeast action.

Aldehydes. *Acetaldehyde*, $\text{CH}_3 \cdot \text{CHO}$.—Other common names are ethyl aldehyde and acetic aldehyde.

1. Formation from Alcohol.—The formation of acetaldehyde and its reduction to alcohol are steps in the theories of fermentation advanced by Schade, Kostytshev, Neuberg and Kerb, and Palladin and Sabinin, which see.

In contradiction to Roeser,² Trillat ³ asserted that oxygen is essential for the formation of acetaldehyde in alcoholic fermentation. Trillat and Sauton ⁴ observed that yeast changes alcohol to acetaldehyde and in time reforms alcohol from the aldehyde; they ⁵ claimed, however, that the acetaldehyde is not formed through the fermentative action, but by mere contact of alcohol and yeast in the absence of sugar.

2. Reduction to Alcohol.—Kostytshev and Hübbenet ⁶ confirmed the formation of alcohol from acetaldehyde by yeast juice and suggested that the latter may be an intermediary in fermentation. According to Kostytshev,⁷ only 20 to 30 per cent of the alcohol is thus formed under certain conditions. Zuckerhandl and Messiner-Klebermass ⁸ claim that the reduction of acetaldehyde to alcohol by yeast is not directly attributable to the dextrose or glycogen, but to the trioses formed from the dextrose.

3. Properties.—Acetaldehyde is a colorless inflammable liquid, with an irritating odor, miscible with water, alcohol, and ether; specific gravity at 15° C. 0.79; boiling point 21° C.

Various Aldehydes.—Neuberg and Steenbock ⁹ observed that yeasts transform *valeraldehyde* into amyl alcohol. Results by Neuberg ¹⁰ with numerous aldehydes confirm his previous report that in general alde-

¹ Biochem. Z. 1914, **62**, 459.

² Ann. inst. Pasteur 1893, p. 41.

³ Compt. rend. 1908, **146**, 645.

⁴ Ibid. 1908, **146**, 996.

⁵ Ann. inst. Pasteur 1910, **24**, 296.

⁶ Z. physiol. Chem. 1912, **79**, 359; 1913, **85**, 408.

⁷ Ibid. 1914, **92**, 402.

⁸ Biochem. Z. 1932, **255**, 330.

⁹ Ibid. 1913, **52**, 493; 1914, **59**, 188.

¹⁰ Ibid. 1918, **88**, 145.

hydes promote alcoholic fermentation of dextrose and mannose by yeast, also that kēto acids, in combination with dipotassium phosphate, act as a coenzyme. The aldehydes employed in his experiments include those of the fatty acids from *formaldehyde* to *decaldehyde*, also *chloral hydrate*, various *aromatic aldehydes* and *aromatic hydroxyaldehydes*, *cyclic aldehydes*, *dialdehydes*, *keto aldehydes*, and *aldehyde acids*. *Cinnamaldehyde*, also included in the list, is of significance, since, being the chief flavoring constituent of cinnamon, it enters into many oven products.

The above results do not imply that the various aldehydes are transition or final products of ordinary fermentation or are constituents of yeast.

Carbohydrates. *Trehalose*, $C_{12}H_{22}O_{11} + 2H_2O$.—Koch and Koch¹ obtained crystalline trehalose from a mixture of ether and alcohol extracts of yeast. Tanret² isolated from 100 grams of dried top yeast 2 grams of trehalose.

According to Myrbäck,³ fresh dry yeast ferments with about equal rapidity both dextrose and trehalose, after the action is well under way. A sample 6 years old, however, fermented trehalose rapidly and dextrose slowly. From the products of fermentation of levulose by dried yeast, Robison and Morgan⁴ isolated the non-reducing *d*-rotatory ester, *trehalose monophosphate*.

Veibel⁵ postulates that *trehalose ester* is synthesized from hexose monophosphate or directly from hexose.

Gentiobiose, $C_{12}H_{22}O_{11}$.—Isaiev⁶ showed that H. Fischer's *isomaltose* is gentiobiose.

Glycogen, $(C_6H_{10}O_5)_n$.—See also p. 479, and Volume III, pp. 283, 359.

Giaja,⁷ in the hydrolysis of the glycogen of yeast killed by boiling, employed the digestive juice of the snail (*Helix pomatia*), since it dissolves the cell membrane, thereby acting more rapidly than pancreatin. In addition to glycogen, the juice dissolved 15 to 21 per cent, dry basis, of carbohydrates other than glycogen, calculated as dextrose. Hydrolysis of the residue from the snail juice digestion yielded 33 per cent of reducing sugar consisting of dextrose and mannose, the

¹ Science 1925, 61, 570.

² Compt. rend. 1931, 192, 1056.

³ Svensk Kem. Tid. 1936, 48, 55.

⁴ Biochem. J. 1928, 22, 1277.

⁵ Biochem. Z. 1932, 252, 305.

⁶ Chem. Listy 1926, 20, 251.

⁷ Compt. rend. soc. biol. 1914, 77, 2; 1919, 82, 719.

same sugars as were obtained in the digestion. Although the fermentative power was largely destroyed, the action on sugar and respirative power were little changed.

Results by Bruschi¹ indicate that glycogen, as found in the yeast cell, is formed by the condensation of an intermediate product of fermentation. According to Brücke,² the amount formed for the same amount of carbon is two to three times as much from dextrose as from alcohol.

Kullberg,³ by moving yeast to a fresh medium after 20 hours' fermentation, increased the glycogen to a maximum of 28 per cent. At the beginning of fermentation it ordinarily decreased, but if previously given a medium rich in mineral salts and sugar it increased. High glycogen content was associated with low nitrogen content, and *vice versa*, which agrees with the experience of Henneberg,⁴ who found little or no glycogen in the presence of more than 53 per cent of protein.

Heiduschka and Schäfer⁵ showed that the glycogen in yeast decreases during storage at first rapidly, then gradually to a constant rate after 10 to 12 days. The loss is due to respiration and not to a change of one carbohydrate into another, although the gum increases as the glycogen decreases.

Mannan (Yeast Gum), $(C_6H_{10}O_5)_n$.—Salkowski⁶ obtained from pressed yeast 5.39 per cent of gum of which 5 to 7 per cent went into solution on fermentation. The maximum gum content in commercial baker's yeast, reported by Stockhausen and Silbereisen,⁷ was 13 per cent. In other yeasts it ranged from 4.4 to 8.9 per cent.

Meigen and Speng⁸ assign the formula $C_{12}H_{22}O_{11}$ to yeast gum, polarizing at $+89.6^\circ$, obtained by Salkowski's method. On hydrolysis, dextrose and mannose were obtained. As prepared and purified by Harden and Young,⁹ yeast gum was a white powder polarizing $+66.76^\circ$ and containing 4.9 per cent of ash. It was not colored by iodine solution and yielded a flocculent precipitate with Fehling solution.

¹ Atti accad. Lincei, 1912, **21**, I, 54.

² Biochem. Z. 1933, **264**, 157.

³ Z. physiol. Chem. 1914, **92**, 340.

⁴ Biedermann's Zentr. 1911, **40**, 277.

⁵ Arch. Pharm. 1934, **272**, 137.

⁶ Z. physiol. Chem. 1910, **69**, 466.

⁷ Wochschr. Brau. 1935, **52**, 257.

⁸ Z. physiol. Chem. 1908, **55**, 48.

⁹ Proc. Chem. Soc. 1912, **28**, 235; J. Chem. Soc. Trans. 1912, **101**, II, 1928.

Kraut and Eichhorn¹ prepared yeast gum by Salkowski's method² and determined its absorption isotherm on orthoaluminum oxide by Willstätter and Kraut's method.³ Analyses of the purified yeast gum corresponded closely with the formula $(C_6H_{10}O_5)_n$; the specific rotation at 20° C. was +88.8°. Kraut, Eichhorn, and Rubenbauer⁴ verified the foregoing results on a preparation obtained by enzymic decomposition. Unsuccessful attempts were made to isolate "*yeast-gummase*," an enzyme which their results indicated as being present.

Hashitani⁵ describes a method of determining yeast gum and glycogen. The gum is not acted on by takadiastase, pancreatin, or invertase. By acid hydrolysis it yields mannose, dextrose, and methyl pentose. By depolymerization with glycerol, α -yeast gum is obtained. The gum does not appear to serve as a reserve substance.

Gorbach and Lerch⁶ have shown that yeast gums differ from tryptophane in not having a region of selective absorption of ultra-violet rays, although the shorter the wave the greater the absorption.

Hemicellulose.—*Yeast cellulose*, a term used by earlier workers to distinguish the cell wall material of yeast from true cellulose, appears to consist of two hemicelluloses. By heating with water under pressure, Salkowski⁷ dissolved *erythrocellulose*, with the specific rotation of +173°; it stained brown with iodine solution and on hydrolysis passed completely into dextrose. The residual cell wall material was named *achroocellulose*; it gave no color with iodine solution and on hydrolysis yielded equal parts of dextrose and mannose.

Meigen and Spreng,⁸ who adopted the names *dextran* and *manno-dextran* for achroocellulose and erythrocellulose respectively, confirm the opinion that yeast contains no true cellulose. They obtained 12.5 per cent of crude cell wall material, staining brown with iodine solution, by treating fresh yeast with portions of 0.25 per cent potassium hydroxide during 6 months, finally drying with alcohol and ether. Although not so stated by the authors, the high percentage suggests contamination with gum or glycogen or both. By acid hydrolysis, dextran to the extent of over half of the crude material was changed to dextrose and by a second hydrolysis more still was so changed. Dextran was also dissolved out by boiling with 15 per cent potassium

¹ Ber. 1927, **60B**, 1639.

² Z. physiol. Chem. 1910, **69** 466.

³ Z. physiol. Chem. 1923, **56B**, 1117.

⁴ Ber. 1927, **60B**, 1644.

⁵ Bul. Agr. Chem. Soc. (Japan) 1927, **3**, 2.

⁶ Biochem. Z. 1931, **235**, 259.

⁷ Ber. 1894, **27**, 3325.

⁸ Z. physiol. Chem. 1908, **55**, 48.

hydroxide to a non-reducing substance differing from yeast gum in rotatory power. The residue (mannodextran) from the hydrolysis, like the achroocellulose of Salkowski, split into equal parts of dextrose and mannose on hydrolysis. Chitin was not present.

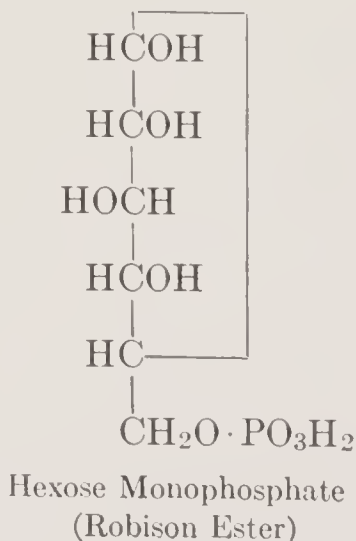
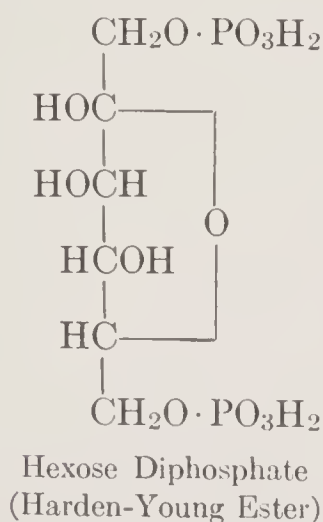
Salkowski¹ states that yeast membrane contains *erythrocellulose*, a soluble cellulose, which yields sugar during autolysis, also *achroocellulose*, an easily hydrolyzable cellulose, similar to that of Iceland moss.

Zechmeister and Tóth² showed that the *polysaccharides* of yeast membrane are formed by a 1,3 coupling of dextrose molecules. From compressed yeast, killed with acetic acid, by successive digestion with pepsin and diastase, and washing with water, alcohol, and ether, they obtained 1.1 per cent of cell wall material consisting of about 80 per cent of polysaccharides soluble in cold concentrated hydrochloric acid and reprecipitated by ice-cold water, alcohol, and ether. No hydrolysis was effected by boiling with water; complete hydrolysis, with formation of dextrose, resulted on boiling with hydrochloric acid. Solution was effected by boiling dilute alkali with destruction of the ability to form dextrose by acid hydrolysis.

Phosphorus-Organic Compounds. *α-Phosphoglycerol; 2- and 3-Phosphoglyceric Acids; Phosphopyruvic Acid; Phosphodihydroxyacetone; Phosphoglyceraldehyde; Triose Monophosphate (Triosemonophosphoric Acid).*—See Meyerhof's Theory, p. 475.

Hexose Diphosphate (Hexosediphosphoric Acid).—See also Harden and Young's Theory, p. 473, and Meyerhof's Theory, p. 475.

The structural formulas given herewith show that the so-called Harden-Young ester and the Robison ester are hexose acid phosphates or, differently expressed, hexosephosphoric acids.



¹ Ibid. 1921, 114, 31.

² Biochem. Z. 1934, 270, 309; 1936, 284, 133.

Young¹ isolated, as the lead salt, hexosediphosphoric acid formed from a soluble phosphate and dextrose, levulose, or mannose by the action of yeast juice. The formula $C_6H_{10}O_4(H_2PO_4)_2$ was confirmed. By hydrolysis, phosphoric acid and levulose are liberated. When it is heated with phenylhydrazine one molecule of phosphoric acid and phenylhydrazine hexosephosphate osazone are formed.

Morgan² prepared from yeast hexosediphosphoric acid the dextro- and levorotatory isomers α - and β -methylhexose diphosphate. Morgan and Robison³ suggest that hexose diphosphate is γ -fructose-1,6-diphosphate. V. Euler and Nilsson⁴ discovered an easily cleavable phosphate in the extract of dried yeast which diminishes within a few hours. Sodium hexose diphosphate retards this loss, and phosphoric acid at first increases the amount.

In comparisons made by Hoffstetter, Leichter, and Nord,⁵ fermentation by living yeast varied in the reaction and relationship between the heat formed and carbon dioxide evolved, whereas in that by maceration juice hexose diphosphate was an actual end product and the heat and carbon dioxide curves ran parallel.

Russ⁶ considers that the ester, which he designates "Harden's acid" or "zymophosphate," is a *maltose tetraphosphate* and cites evidence as follows: (1) like maltose, it has only 46 per cent of the reducing power of an equivalent amount of dextrose, (2) it is formed during the direct fermentation of maltose, and (3) it is converted by horse kidney phosphatase into the Robison ester which he claims is maltose diphosphate. He gives the following fermentation scheme: sucrose \rightarrow maltose \rightarrow maltose diphosphate \rightarrow maltose tetraphosphate.

Hexose Monophosphate (Hexosemonophosphoric Acid).—In the filtrate from hexosediphosphoric acid, after synthesis from levulose and disodium hydrogen phosphate, Harden and Robison⁷ obtained a *d*-rotatory aqueous solution of an acid believed to be hexosemonophosphoric acid. Later Robison⁸ prepared a mixture of the mono- and diphosphoric acids from which the monophosphoric was isolated.

Adenylic Acid, $(HO)_2OP \cdot O \cdot C_5H_8O_3 \cdot C_5H_4N_5$.—See Vol. III, p. 285.

¹ Proc. Roy. Soc. London 1909, (B), **81**, 528; Biochem. Z. 1911, **32**, 177.

² Biochem. J. 1927, **21**, 675.

³ Ibid. 1928, **22**, 1277.

⁴ Z. physiol. Chem. 1931, **195**, 273.

⁵ Biochem. Z. 1938, **295**, 414.

⁶ Österr. Chem.-Ztg. 1938, **41**, 194.

⁷ Proc. Chem. Soc. 1914, **30**, 16.

⁸ Biochem. J. 1922, **16**, 809.

Schmidt¹ was the first to show that an enzyme in rabbit muscle causes deamination of the adenylic acid of muscle with formation of inosic acid, but not that of yeast. The two adenylic acids were judged to be isomers. Other differences in yeast and muscle adenylic acids, brought out by Embden and Schmidt,² are respectively as follows: melting point (with decomposition) 193 to 194° and 197 to 200° C.; difficultly soluble in hot water, readily soluble; specific rotation at 20° C. in 2 per cent sodium hydroxide -56° and -47.5° , at 20° C. in 10 per cent hydrochloric acid -36.5° and -26° ; not converted by nitric acid into inosic acid, converted into inosic acid. The yeast form is more rapidly hydrolyzed with liberation of phosphoric acid and on decomposition by steam distillation with hydrochloric acid yields more furfural than the muscle form.

Because muscle adenylic acid has been isolated from yeast and yeast adenylic acid from pancreas, Lindner³ suggests, as more appropriate, the names *synadenylic acid* and *ergadenylic acid* respectively.

Adenosine Triphosphate (Adenosinetriphosphoric Acid).—Wagner-Jauregg⁴ obtained from fresh yeast adenosine triphosphoric acid, inorganic pyrophosphate, and what was judged to be *inosinepyrophosphoric acid*.

Schäffner and Krumy⁵ postulate that fermentation without new phosphorylation may take place in the presence of sufficient organic phosphate, the phosphopyruvic acid first formed from hexose diphosphate reacting with adenylic acid to form pyruvic acid and adenosine triphosphate, and the latter with glucose to reform hexose diphosphate and adenylic acid.

According to Gibaylo and Umschweif,⁶ *adenosinetriphosphoric acid*, when hydrolyzed with alkali, yields *tetraphosphoric acid*, not pyrophosphoric acid, which was isolated from yeast extract and identified.

Inosine Pyrophosphate.—See Adenosine Triphosphate.

Lecithin and Cephalin.—Austin⁷ reports that a lot of baker's yeast contained total fat 4.5 and crude phospholipins (phosphatides) 0.5 per cent. A lecithin and cephalin fraction had a nitrogen : phosphorus

¹ Z. physiol. Chem. 1928, **179**, 243.

² Ibid. 1929, **181**, 130.

³ Ibid. 1933, **218**, 12.

⁴ Ibid. 1936, **238**, 129.

⁵ Ibid. 1936, **243**, 149.

⁶ Compt. rend. soc. biol. 1937, **125**, 275.

⁷ J. Biol. Chem. 1924, **59**, lii.

ratio of 1 : 1. By hydrolysis, choline, cholamine, and unidentified nitrogenous substances were obtained.

Since the phosphatides cannot be separated from yeast except after autolysis, Grafe¹ concludes that they form a complex with the protein.

Among the water-soluble constituents obtained by Newman and Anderson² in the hydrolysis of yeast phospholipides were *glycerophosphoric acid*, *choline*, and *aminoethanol*. The saturated acids consisted of 50 per cent each of palmitic and stearic acids and constituted 14 per cent of the total acids; the unsaturated acids, on reduction, consisted of 60 per cent palmitic and 40 per cent stearic acids, together with a trace of lauric acid. Probably no acid of a higher degree of unsaturation than oleic was present in the liquid acids. Judging from the ratio of amino nitrogen to total nitrogen, 4 parts of lecithin to 1 part of cephalin were present.

Salisbury and Anderson³ purified yeast *lecithin* until free from amino nitrogen and yeast *cephalin* until all the nitrogen was in NH_2 combination. In both, a yield of about 64 per cent of fatty acids consisting of 84 to 86 per cent of liquid acids was obtained. The solid acids were palmitic and stearic. The glycerophosphoric acid separated by hydrolysis from lecithin was optically active, that from cephalin inactive. Choline and aminoethyl alcohol respectively were the other water-soluble products.

A water-soluble phosphatide, dialyzed by Gutstein⁴ from yeast and peas, gave both oxidase and reductase reactions.

Nucleic Acid.—See also formulas, Volume III, p. 287.

Results obtained at the Fleischmann Laboratories show a yield of 0.75 per cent of nucleic acid (magnesium nucleinate 1 per cent). Occasionally much higher results are obtained.

Historical.—Levene and Bass,⁵ in their exhaustive monograph, divide the work on nucleic acids into three periods: (1) discovery (Miescher; Altmann); (2) classification and components (Kossel et al.); and (3) structure (American school). Part I of the monograph is devoted to Components of Nucleic Acids and Part II to Nucleic Acids. The contributions of Levene, leader of the American school, and his associates have clarified our knowledge of one of the most intricate groups in biochemistry.

¹ Biochem. Z. 1929, **205**, 256.

² J. Biol. Chem. 1933, **102**, 229.

³ Ibid. 1936, **112**, 541.

⁴ Biochem. Z. 1929, **207**, 177.

⁵ Nucleic Acids, New York, 1931.

Miescher,¹ the pioneer, after mastering structural and physiological details of cell nuclei, turned his attention to the chemical constituents of the nuclear substance of pus. His first paper was so startling in its revelations that Hoppe-Seyler deferred publication until he and his students could verify the conclusions. Even when Miescher's dependability was well established, Hoppe-Seyler withheld a proposed plan of investigation which after Miescher's death led to rich returns. Hoppe-Seyler, following Miescher's methods, extended the work so as to cover *yeast nucleic acid* and other plant nucleic acids. Other substances yielding nucleic acids in the hands of Miescher, Hoppe-Seyler, and Altmann² were casein, egg yolk, thymus gland, and salmon sperm. The term nucleic acid was introduced by Altmann.

The constituents of nucleic acids belong in the following groups: sugars, purines, pyrimidines, and phosphoric acids. Three progressive definitions aid in understanding the structure of the group: (1) nucleosides are glucosides of purines and pyrimidines; (2) nucleotides are phosphoric esters of nucleosides; (3) nucleic acids are polynucleotides, that is, unions of several nucleotides, the junctions being phosphoric acid radicals to sugar radicals.

The work of Levene and Tipson³ and of Bredereck⁴ indicates that all the ribose residues of yeast nucleic acid have the furanose ring structure.

Properties.—Nucleic acids are characterized by their insolubility in alcohol and dilute acids and their solubility in alkaline solutions. They are slightly soluble in water to a cloudy liquid. Their acidity is greater than that of the proteins.

They give negative protein tests and do not reduce Fehling solution, but are strongly dextrorotatory. Steudel⁵ suggests that the change in rotation during aging of yeast nucleic acid may be due to the tightening of the sugar linkage.

Nucleates.—The term *nucleins*, formerly loosely applied to nucleic acid and its protein esters (*nucleates*), is now generally restricted to the latter; it might well be abandoned entirely. Animal nucleic acid exists in nature combined with histones or protamines such as salmin or clupein, forming the bulk of the *chromatin* of the biologists, but in-

¹ Hoppe-Seyler's Med. Chem. Unters. 1871, p. 441; Die histochem. u. physiol. Arbeiten v. Friedrich Miescher, Leipzig, 1897.

² Arch. Anat. Physiol., Physiol. Abt. 1889, p. 524.

³ J. Biol. Chem. 1932, **94**, 809; **97**, 491.

⁴ Ber. 1932, **65B**, 1830; 1933, **66B**, 198.

⁵ Z. physiol. Chem. 1930, **188**, 203.

formation is lacking on the exact nature of the proteins combined with yeast nucleic acid. The removal of such protein matter is essential in purifying crude nucleic acid.

Sulphur-Organic Compounds. *Glutathione*.—See also Volume III, p. 274.

By the Hopkins method,¹ Pirie² obtained a yield of 0.1 per cent of glutathione from yeast; by a modification of the method, Kozlowski³ prepared a crystalline copper compound from the oxidized glutathione of baker's yeast. Régnier⁴ prepared very pure glutathione from beer yeast by successive precipitation as lead and copper compounds, decomposing the latter with hydrogen sulphide.

The following figures were obtained at the Fleischmann Laboratories:

GLUTATHIONE IN YEAST

	Yeast solids	Glutathione (dry basis)
	%	%
Baker's yeast:		
I Fresh.....	30.87	1.01
II Fresh.....	30.72	0.82
Brewer's yeast:		
I Fresh.....	27.20	0.67
In refrigerator 4 days.	27.20	0.63
II Fresh.....	29.87	0.93
Autolyzed 70 hours, 25° C..	29.87	0.41

Adenyl Thiopentose.—Suzuki, Odake, and Mori⁵ isolated from yeast a basic compound $C_{11}H_{15}N_5O_3S$, that may have been adenyl thiomethylpentose. The alcohol extract of yeast was found by Suzuki and Mori⁶ to contain a thiosugar with the probable formula $O \cdot CHOH \cdot CHOH \cdot CHOH \cdot CHCH_2S \cdot CH_3$. The same substance was prepared by the acid hydrolysis of adenyl thiomethylpentose.

¹ J. Biol. Chem. 1929, **84**, 269.

² Biochem. J. 1930, **24**, 51.

³ Biochem. Z. 1931, **241**, 403; **242**, 249; Science 1934, **79**, 388.

⁴ Compt. rend. soc. biol. 1933, **112**, 526.

⁵ Biochem. Z. 1924, **154**, 278.

⁶ Ibid. 1925, **162**, 413.

Thiamin (Vitamin B).—In the experience of Seidell,¹ rupturing the walls of the yeast cells by heat, drying, or grinding is essential for proper extraction of vitamin B.

In 5 samples of yeast, Quinn, Whalen, and Hartley² observed that the vitamin B content showed variation of tenfold, while the vitamin G content was very uniform.

Crystalline vitamin B hydrochloride prepared by the method of Jansen and Donath,³ as examined by R. R. Williams, Waterman, and Gurin,⁴ retarded polyneuritis but not loss in weight. R. J. Williams and Roehm⁵ found it an effective stimulant for yeast growth.

Windaus, Tschesche, Ruhkopf, Laquer, and Schultz⁶ prepared crystalline vitamin B₁ from yeast with lower activity than that of Jansen.⁷ From rice bran, Van Veen⁸ obtained crystalline vitamin B₁ agreeing in characters with that made by Windaus from yeast. The formulas derived by the two authors are C₁₂H₂₀O₂N₄S and C₁₂H₁₇ON₃S respectively.

Judging from tests with rats by Walker and Nelson,⁹ fresh compressed yeast contains only half as much vitamin B as dried compressed yeast, both calculated to the same basis.

By oxidation, Peters¹⁰ converted thiamin into a substance with blue fluorescence in ultra-violet light. He suggests that the Bence-Jones *quinoidine* in yeast extracts may be derived from both B₁ and B₂.

Itter, Orent, and McCollum¹¹ use gaseous hydrochloric acid in absolute methyl alcohol as a solvent for vitamins B₁ and B₂.

Lassen¹² describes a strain of bottom yeast, cultivated 18 months by moving from one vitamin-B-free medium to another, that was able to synthesize B₁ and B₂ in such a medium.

Colors and Related Substances. *Flavin (Vitamin G or B₂).*—Yeast is rich in flavin (classed here with colors), thus, as noted by

¹ Rec. trav. chim. 1929, 48, 855.

² J. Nutrition 1930, 3, 257.

³ Geneeskund. Tijdschr. Nederland. Indië 1927, 66, 810.

⁴ J. Biol. Chem. 1930, 87, 559.

⁵ Ibid. p. 581.

⁶ Z. physiol. Chem. 1932, 204, 123.

⁷ Biochem. J. 1930, 24, 1824.

⁸ Z. physiol. Chem. 1932, 208, 125.

⁹ Am. J. Physiol. 1933, 103, 25.

¹⁰ Nature 1935, 135, 107.

¹¹ J. Biol. Chem. 1935, 108, 571.

¹² Acta Path. Microbiol. Scand. 1936, 13, 309.

Frey,¹ being in the class with meat, milk, and eggs. Quantitative results, other than by animal experimentation, are, however, meager. Now that the constitution of the substance is known, suitable analytical methods will doubtless soon be devised. According to V. Euler, Adler, and Schlötzer,² about 15 per cent of the total flavin of yeast press juice consists of the soluble form. Pett³ brought out that yeasts with high fermenting power have also high flavin content.

Thiochrome.—Kuhn, Wagner-Jauregg, Van Klaveren, and Vetter⁴ observed that the fluorescence of crude lactoflavin changes from yellow to blue on addition of alkali. This is due to thiochrome, a sulphur-containing pigment differing in formula from *thiamin* (B₁) by only two hydrogens. It is convertible by hydrogenation into *dihydrothiochrome*, which probably is identical with thiamin.

Hemochromogen Pigments.—It has been abundantly demonstrated by Keilin, Hans Fischer, V. Euler, Schumm, Coolidge, and others that yeast contains pigments analogous to, if not identical with, those of blood. The arbitrary classification of the data in three groups—hematin and hemin, porphyrin, and cytochrome—is for convenience in reference.

1. Hematin and Hemin.—H. Fischer,⁵ in *Saccharomyces anamensis* as well as common yeast grown on beer wort, established the presence of *hemin* and only traces of coproporphyrin. Direct synthesis from sugar and mineral matter is believed to take place. The hemochromogen spectrum in the pyridine extract was obtained. Porphyratin, separated by Schumm⁶ from distillery yeast, showed a pure hematin spectrum, preformed porphyrin being absent.

Schumm and Mertens⁷ emphasize the correspondence of *hematin* from animals and higher groups of plants. They state that yeast synthesizes *iron porphyratin* with a constitution the same as hematin.

Fischer and Schwerdtel⁸ prepared crystalline *hemin* from yeast. The steps were plasmolyzing with saturated salt solution, treatment with pyridine, extraction with ether, precipitation with water, and crystallization. They state that this is the first actual demonstration that this pigment occurs in plants.

¹ Ind. Eng. Chem. 1930, **22**, 1154.

² Z. physiol. Chem. 1934, **226**, 87.

³ Biochem. J. 1935, **29**, 937.

⁴ Z. physiol. Chem. 1935, **234**, 196.

⁵ Ibid. 1926, **152**, 144.

⁶ Ibid. 1926, **159**, 192.

⁷ Ibid. 1927, **170**, 1.

⁸ Ibid. 1928, **175**, 248.

2. Porphyrins.—Porphyrin, being present in yeast, but absent in leaves as examined by Fischer and Schneller,¹ is considered by them to antedate hemin in evolution.

Fischer and Hilger² in 1924 announced that yeast by acid hydrolysis yields *hematoporphyrin* and by autolysis or putrefaction *coproporphyrin* and Kämmerer's *porphyrin*. Since fresh yeast contains only a trace of porphyrin, the ash contains iron, and autolyzed yeast, after removal of the porphyrin, shows the hemin spectrum, they assume *hemoglobin* to be present. Later Fischer and Fink,³ observing special precautions, detected only *coproporphyrin*. The occurrence of this substance, glycogen, and glucosamine, the synthesis of amino acids from keto acids, and the analogy of pancreatic and yeast antitrypsin, taken together, suggest a close relationship between yeast and lower animal types. H. Fischer and Fink⁴ demonstrated the synthesis of *coproporphyrin* by using cocoanut milk or extract of shredded cocoanut as medium.

V. Euler, Fink, and Nilsson⁵ note that the lack of oxygen causes the formation of *coproporphyrin*. In bottom yeast this retarded the washing out of coenzymes. In top yeast the coenzymes were not washed out whether or not aerated.

By addition of *coproporphyrin* to the medium, V. Euler and Fink⁶ increased ten to thirtyfold the content of that substance in the yeast (copro-yeast). The treatment decreased the sucrase in top yeast, but increased it in bottom yeast, whereas glycogen was increased to the same amount in both.

3. Cytochrome.—The hemochromogen pigment cytochrome, an intracellular respiratory catalyst, according to Keilin,⁷ is widely distributed in plants and animals. The substance consists of three hemochromogen compounds, each yielding a hemochromogen that combines with O₂ and CO, but is not classed with muscle hemoglobin. According to Schumm,⁸ cytochrome contains a *porphyrin* and is the second porphyrin carrier, chlorophyll excepted, found in plants. The author does not, however, think H. Fischer justified in concluding that yeast

¹ Ibid. 1924, **135**, 253.

² Ibid. 1924, **138**, 288.

³ Ibid. 1924, **140**, 57.

⁴ Ibid. 1925, **150**, 243.

⁵ Ibid. 1926, **158**, 302.

⁶ Ibid. 1927, **162**, 242.

⁷ Proc. Roy. Soc. (London) 1925, **98B**, 312.

⁸ Z. physiol. Chem. 1926, **154**, 171, 314.

contains a blood pigment. Zeile and Reuter¹ demonstrated that yeast cytochrome is a complex of a *hemin* and a *porphyrin*, with a colloidal vehicle. The porphyrin is a derivative of *etioporphyrin* III, the side chain being like that of natural blood pigment.

Keilin² attributes peroxidase activity to cytochrome and related substances. V. Euler, Fink, and Hellström³ correlate cytochrome with catalase activity. Coolidge,⁴ however, states that it may not be cytochrome, but the accompanying iron complex, that acts as a catalyst. Meldrum⁵ asserts that the glutathione of yeast neither reduces cytochrome nor takes part directly in the oxidation of carbohydrates.

Keilin² observed that the reduced form has four bands in the absorption spectrum at 6046, 5665, 5502, and 5210 A.U.; the oxidized form shows no absorption bands, but faint shading at 520 to 540 and 550 to 570. Yakushiji and Mori⁶ synthesized cytochrome from yeast protein and hemochromogen that was identical with that isolated from yeast. They suggest the following system: oxygen, cytochrome *c*, cytochrome *b*, codehydrogenase, dehydrogenase, substrate. V. Euler and Fink⁷ determined the cytochrome in the pyridine extract of yeast by comparison of the density of the hemochromogen shown in a photo-spectrograph with that of standard hemochromogen. V. Euler and Hellström⁸ found that the cytochrome of yeast has three absorption bands, that from blood only two. The behavior of the third band suggests that it belongs to another substance.

By saturating with ammonium sulphate an alkaline extract of yeast, Coolidge⁹ precipitated protein and cytochrome "C," together with an iron complex, with no visible spectrum, which can be separated by ultra-filtration, since it remains in solution when the protein and cytochrome are precipitated by trichloroacetic acid. The oxidation potential of the iron complex is near that at which the cytochrome spectrum is visible.

Elion¹⁰ reviews the work on the absorption spectra of reduced cytochrome from baker's yeast.

¹ Ibid. 1933, **221**, 101.

² Proc. Roy. Soc. (London) 1925, **98B**, 312.

³ Ibid. 1927, **169**, 10.

⁴ J. Biol. Chem. 1932, **98**, 755.

⁵ Biochem. J. 1930, **24**, 1421.

⁶ Acta Phytochim. (Japan) 1937, **10**, 113.

⁷ Z. physiol. Chem. 1927, **164**, 69.

⁸ Ibid. 1930, **190**, 189.

⁹ Nature 1931, **128**, 223.

¹⁰ Bul. soc. chim. biol. 1936, **18**, 165.

V. Euler, Fink, and Hellström¹ found that the content of cytochrome of dried top yeast is almost as high as that of the fresh yeast, on the same basis, which is not true of bottom yeast. There is little variation in the hemochromogen content of top and bottom yeast, which is not true of cytochrome.

Riboflavin (Vitamin G or B₂).—See also Thiamin above.

Block and Farquhar² failed to destroy the vitamin by heating dry yeast for 4 weeks at 95 to 100° C. or treating with alkali in the cold.

Pett³ showed that phosphate is essential for flavin development. Potassium cyanide in proper proportion poisons iron-containing catalysts and increases the flavin content. Autolysis reduces the flavin content only slightly; forced aerobic utilization of the glycogen causes it to disappear rapidly.

Enzymes and Coenzymes, in bewildering number, have been identified in yeast.

Catalase.—According to V. Euler and Blix,⁴ catalase action is increased by adding sucrose, asparagine, potassium phosphate, and magnesium phosphate.

Nakamura⁵ calculates that yeast catalase should be many times as stable as it appears to be at 17° C., if temperature alone brings about its change in stability, hence he concludes that there are other disturbing influences. Matsuyama⁶ gives pH 6.3 and 22° C. as optima for top yeast catalase.

The results given by Murakami⁷ on the action of monochromatic light in stimulating catalase show that the intensity rather than the wave length is the chief factor.

Proteinases (Proteases) and Peptidases.—Dernby⁸ names three proteinases, corresponding to animal enzymes, which are active in yeast autolysis, as follows: (1) *yeast pepsin*, optimum pH 4 to 4.5, changes proteins into peptones; (2) *yeast tryptase*, optimum pH 7, changes acid albumin, gelatin, and caseinogen into peptides and amino acids; and (3) *yeast ereptase*, optimum pH 7.8, changes peptones and

¹ Z. physiol Chim. 1927, **169**, 10

² J. Biol. Chem. 1933, **103**, 643.

³ Arkiv Kemi, Mineral. Geol. 1935, **11B**, No. 53.

⁴ Medd. K. Vetenskapsakad. Nobelinst. 1919, **5**, No. 23, 1.

⁵ Z. physiol. Chem. 1924, **139**, 140.

⁶ J. Faculty Agr. Hokkaido Imp. Univ. 1933, **32**, 109.

⁷ J. Agr. Chem. Soc. Japan 1937, **13**, 429, 435.

⁸ Biochem. Z. 1917, **81**, 109.

polypeptides into amino acids. Willstätter and Grassmann¹ found only trypsin and erepsin with optimum pH 5 to 6 and 7.8 respectively.

Grassmann and Dyckerhoff² advocate the abandonment of the terms "yeast erepsin" and "yeast trypsin" of Dernby in favor of (1) *proteinase*, (2) *dipeptidase*, and (3) *polypeptidase*. They found only one proteinase, not two (erepsin and trypsin). They note the following differences between (2) and (3): *dipeptidase*, freed from polypeptidase and protease, hydrolyzes *dl*-alanylserine, *l*-leucyl-*d*-glutamic acid, and *d*-alanyl-*l*-tyrosine, but not certain polypeptides; *polypeptidase*, freed from dipeptidase, hydrolyzes certain polypeptides, also a number of poly- and dipeptide esters; it does not attack proteins.

Blagoveshchenskii and Vovchenko³ give 40 to 45° C. as the optimum activation temperature. Grassmann, Klenk, and Peters-Mayr⁴ studied the dipeptidases of yeast with different substrates.

Grassmann and Bayerle⁵ describe the *dipeptidase* and *aminopolypeptidase* of yeast, the former acting on *dipeptides* in which the NH₂ group of either asparagine or aspartic acid is combined with another amino acid, the latter on *glycylglycyl-l-asparagine*. From English top yeast, Macrae,⁶ by autolysis, obtained preparations of *dipeptidase* free from protease, and *amino-polypeptidase* free from dipeptidase and protease. Grassmann and Dyckerhoff⁷ explain the action of yeast *polypeptidase*, prepared by a simplified method, on the tripeptides *leucylglycylglycine* and *glycylglycylleucine* and on the tetrapeptides *leucyldiglycylglycine* and *triglycylglycine*.

Aminopolypeptidase.—Grassmann, Embden, and Schneller⁸ describe a process for the preparation of aminopolypeptidase from fresh yeast.

Asparaginase.—An enzyme, discovered by Kurono⁹ in beer and sake yeasts, splits off ammonia from *asparagine* but not from urea, leucine, formamine, or butylamine.

Grassmann and Mayr¹⁰ describe the extreme sensitiveness of yeast

¹ Z. physiol. Chem. 1926, **153**, 250.

² Ibid. 1928, **179**, 41; Ber. 1928, **61B**, 656.

³ Biochem. Z. 1935, **276**, 289.

⁴ Ibid. 1935, **280**, 307.

⁵ Ibid. 1934, **268**, 214.

⁶ Biochem. J. 1933, **27**, 1229.

⁷ Z. physiol. Chem. 1928, **175**, 18.

⁸ Biochem. Z. 1934, **271**, 216.

⁹ J. Col. Agr. Tokyo 1912, **1**, 295.

¹⁰ Z. physiol. Chem. 1933, **214**, 185.

asparaginase to acid and state that it hydrolyzes only *l*- β -asparagine and the diamide of aspartic acid.

Endotryptase.—Buchner and Haehn¹ claim that endotryptase is present in yeast cells. If allowed to act alone, this would destroy zymase, which they regard as a protein. Normally, however, anti-tryptase (antiprotease) protects zymase.

Lipase.—Gorbach and Günter² give pH 6.6 to 6.8, 30° C., and 40 minutes as the optima for yeast *lipase*. Pressed yeasts are richer in lipase than beer yeasts, and pure cultures are more active than commercial yeasts.

Carboxylase.—Neuberg and Karczag³ name the enzyme that is responsible for sugar-free fermentation carboxylase, mediums containing *pyruvic* and *oxymaleic acids* being especially favorable for its action. *Acetaldehyde* was identified as the final link in the chain. Neuberg and Rosenthal⁴ point out that carboxylase differs from *zymase* in that it is destroyed neither by heating at 50° C. nor by addition of chloroform and that it starts the evolution of carbon dioxide in a short time. Neuberg and Czapski⁵ found more carboxylase in bottom than in top yeast. Neuberg and Iwanoff⁶ state that it is not attacked by certain poisons that destroy the activity of zymase.

Palladin, Sabinin, and Lovchinovskii⁷ and Palladin and Sabinin⁸ divide the decomposition of potassium lactate by dead yeast in the presence of a hydrogen-fixing substance into (1) the formation of *pyruvic acid* by *reductase*, (2) the splitting of *pyruvic acid* into carbon dioxide and *acetaldehyde* by carboxylase, and (3) the formation of *alcohol* by reduction of *acetaldehyde*.

Hägglund and Ahlbom⁹ regard the theory that carboxylase is a component of *zymase* as helpful to an understanding of fermentation, assuming that the natural pyruvic acid is identical with the synthetic or is made so by a coenzyme. Alteration of the relative rapidity of fermentation of pyruvic acid and dextrose is questionable evidence.

Cocarboxylase.—As isolated by Lohmann and Schuster¹⁰ from the

¹ Biochem. Z. 1910, **26**, 171.

² Monatsh. 1932, **61**, 47.

³ Biochem. Z. 1911, **36**, 68, 76.

⁴ Ibid. 1913, **51**, 128.

⁵ Ibid. 1914, **67**, 9.

⁶ Ibid. 1914, **67**, 1.

⁷ Bul. Acad. Sci. Petrograd 1915, p. 701.

⁸ Biochem. J. 1916, **10**, 183.

⁹ Biochem. Z. 1927, **181**, 158.

¹⁰ Naturwissenschaften 1937, **25**, 26; Biochem. Z. 1938, **294**, 188.

boiled juice of fresh beer yeast, cocarboxylase has the formula $C_{12}H_{21}O_8N_4P_2SCl$. Although a diphosphate ester of thiamin, it does not have vitamin B activity. It acts in conjunction with a magnesium or manganese salt, hexose, diphosphate, adenosine pyrophosphate, and a coenzyme. In suitable quantity it triples the carbon dioxide production from pyruvic acid.

Dehydrase.—Bernheim¹ established that the enzyme causes the formation of pyruvic acid from lactic acid.

Dehydrogenase (Reductase).—The data on this group of enzymes, involving decolorization of methylene blue, are somewhat extensive, but somewhat confused. L'vov² regards the action of reductase, whereby 2 atoms of the hydrogen of sugar or ionized water are activated, as the first stage of fermentation.

V. Euler and Nilsson³ note the presence of a "co-reductase" (dehydrogenase) in crude cozymase of yeast. Addition of "biocatalyst Z" greatly hastens the decoloration of the dye. *Sodium zymophosphate* serves well as a hydrogen donor, but sodium succinate does not. The reaction velocity in decolorizing methylene blue depends on the amount of yeast and the concentration of the dye and coreductase. V. Euler⁴ discusses the relation of cozymase to yeast dehydrogenases. Studies on dehydrogenases are reported by Sonderhoff,⁵ involving alcohol, acetaldehyde, glyceraldehyde, and acetic, pyruvic, lactic and citric acids.

V. Euler, Nilsson, and Runehjelm⁶ show that methylene blue reduction, although highly instructive, and enzymic oxidation are not parallel reactions; they do, however, find a parallelism of profound significance between the cytochrome content of the yeast and the respiratory power. Lactic acid may be attacked by reductase without coenzyme participation.

V. Euler, Adler, and Eriksen⁷ have studied *glutamic acid dehydrogenase*.

Lactic Acid Dehydrogenase.—This dehydrogenase, obtained from yeast by Hahn, Fishbach, and Niemer,⁸ converts lactic acid ($CH_3 \cdot HCOH \cdot COOH$) into pyruvic acid ($CH_3 \cdot CO \cdot COOH$). As later pre-

¹ Biochem. J. 1928, **22**, 1178.

² Bul. Acad. Imp. Sci. St. Petersburg 1913, p. 501.

³ Z. physiol. Chem. 1925, **149**, 44; 1926, **151**, 155; **152**, 264; **162**, 72.

⁴ Ergebnisse Enzymforsch. 1934, **3**, 135.

⁵ Ibid. p. 163.

⁶ Z. physiol. Chem. 1927, **169**, 123.

⁷ Ibid. 1937, **248**, 227.

⁸ Z. Biol. 1932, **93**, 121.

pared by Hahn and Fischbach,¹ employing the alumina adsorption method, it acted on lactic acid *in vacuo* in the presence of methylene blue, producing pyruvic acid and acetaldehyde. In the experience of Hahn, Niemer, and Freytag,² yeast juice, rich in lactic acid dehydrogenase, failed to act in the presence of oxygen, methylene blue acting as the carrier.

Boyland and Boyland³ fix the optimum *pH* of yeast lactic acid dehydrogenase at 6.4. Unlike the heart enzyme (optimum *pH* 9.3), it acts independent of the coenzyme and does not attack malate. Adler and Michaelis⁴ have shown that lactic acid dehydrogenase from yeast requires no complement for the anaerobic reaction, although addition of an intermediate acceptor is essential for the aerobic.

Alcohol Dehydrogenase.—Wieland and Wille⁵ state that in the dehydrogenation of alcohol, by alcohol dehydrogenase in the presence of an excess of alcohol, the acetic acid first produced is later oxidized, but the amount of carbon dioxide recoverable is less than theory owing to possible combination with proteins and amino acids of the yeast.

Alcohol dehydrogenase may be prepared from dry yeast by the method of Lehmann.⁶ Like glycerophosphoric acid dehydrogenase, it is active only in the presence of coenzyme (*adenosine triphosphate*). Its optimum activity, according to Müller,⁷ is between *pH* 7.5 and 10. V. Euler and Martius⁸ explain the action of yeast dehydrogenase whereby hydrogen is transferred, in descending order of rapidity from ethyl alcohol, through lactic acid, lactyl glycine, and ethyl lactate, to methylene blue, causing discoloration.

Müller⁹ describes an alcohol dehydrogenase in beer yeast that oxidizes propyl alcohol to dimethylketone (acetone).

Codehydrogenase.—V. Euler¹⁰ explains the action of coenzymes, including codehydrogenases. Under anaerobic conditions, the codehydrogenase removes H_2 from the donor system and adds it to the acceptor system. Reoxidation is effected by means of a suitable color

¹ Ibid. 1934, 95, 155.

² Ibid. 1935, 96, 253.

³ Biochem. J. 1934, 28, 1417.

⁴ Z. physiol. Chem. 1935, 235, 154.

⁵ Ann. 1933, 503, 70.

⁶ Biochem. Z. 1934, 272, 95.

⁷ Ibid. 1934, 268, 152.

⁸ Arkiv. Kemi, Mineral., Geol. 1935, 11B, No. 22.

⁹ Biochem. Z. 1933, 262, 239.

¹⁰ Angew. Chem. 1937, 50, 831.

enzyme, the colorless form of which is restored in color by either O_2 or a catalyst of the cytochrome type.

Aldehydease.—Aldehydes are reduced to alcohols by aldehydease.

Rona¹ describes the reduction by yeast of *cinnamic aldehyde*, the chief flavoring constituent of cinnamon and cassia, to *cinnamic alcohol*. Neuberg and Ringer² report reduction of *dl-valeraldehyde* to *l-amyl-alcohol*, Neuberg and Kerb,³ reduction of *citral* to *geraniol* and *acetaldol* to β -butyleneglycol.

Carboligase.—Neuberg and Hirsch⁴ discovered in yeast this enzyme which causes equal molecules of acetaldehyde and benzaldehyde to combine, forming a ketone alcohol. The reaction thus catalyzed is of a type not previously reported. It does not take place except during alcoholic fermentation.

Neuberg and Liebermann⁵ found a factor in yeast that causes decomposition of *o-chlorobenzaldehyde* with formation of the corresponding chloroketoalcohol $C_6H_4(Cl)CHOH \cdot CO \cdot CH_3$ in the presence of starch.

Invertase (Sucrase).—The first name indicates the chemical action, namely inversion, the second the substance inverted, namely sucrose. Emil Fischer's belief that neither *sucrose* nor *maltose* fermented directly, but only after inversion by invertase, has been disputed by Bertrand and Rosenblatt,⁶ Willstätter and Steibelt,⁷ and Willstätter and Lowry.⁸ Cohn,⁹ however, presents evidence in support of Fischer's theory. Probably both processes go on at the same time.

1. Preparation.—Euler and Cramer¹⁰ attributed the formation of invertase in yeast to substances, notably *mannose*, other than sucrose and its derivatives.

Salkowski¹¹ claimed to have separated *gum* from sucrase by dialyzing, but Svanberg¹² was unable to separate the two by this means. V. Euler and Svanberg¹³ concluded that the enzyme consists chiefly

¹ Biochem. Z. 1914, **67**, 137.

² Ibid. 1918, **90**, 388.

³ Ibid. 1918, **92**, 96, 111.

⁴ Ibid. 1921, **115**, 282.

⁵ Ibid. 1921, **121**, 311.

⁶ Ann. inst. Pasteur 1912, **26**, 321.

⁷ Z. physiol. Chem. 1921, **115**, 211.

⁸ Ibid. 1925, **150**, 287.

⁹ Ibid. 1927, **168**, 92.

¹⁰ Biochem. Z. 1913, **58**, 467.

¹¹ Z. physiol. Chem. 1909, **61**, 124; 1921, **114**, 307.

¹² Ibid. 1920, **109**, 65; 1921, **112**, 104.

¹³ Ibid. 1920, **110**, 175.

of carbohydrate, since it remained stationary at a certain point after dialyzing.

The method adopted by Josephson¹ for preparing pure invertase was a combination of principles previously followed separately, namely autolysis, precipitation with alcohol, absorption on kaolin, solution, dialysis, and repetition of the treatment.

2. Properties.—V. Euler and Svanberg² give 26 to 30° C. as the optimum temperature for invertase activity; at 35° C. activity is inhibited. The optimum pH is 6 to 7; at pH 2, the enzyme is destroyed. As calculated by Kertesz,³ the Arrhenius heat-tone constant A is 11,800 at 0°, 63,000 at -3.75°, and only 1400 at -6.25° C. At low acidity (pH 6.7), Nelson and Palmer⁴ were able to pass 13 to 14 per cent of the invertase through a collodion membrane, but in a more acid solution (pH 4.6) only a trace, although the amount left in the bag showed an appreciable loss.

In studying the action of yeast invertase, Quastel and Yates⁵ found that sucrose competes with both *acid* and *basic dyes*, whereas dextrose competes with basic dyes to a greater extent than with acid dyes. The reverse is true of fructose.

Invertase, although considered a proteinlike substance, was shown by V. Euler and Josephson⁶ to be little affected by autolysis or by digestion with pepsin or pancreatin.

3. Influence of Various Factors.—Meisenheimer, St. Gambarjen, and Semper⁷ increased the invertase content of beer yeast eightfold by mixing with sucrose and fermenting 1 to 2 days.

Miller⁸ states that the alcohol extract of yeast stimulates the growth of yeast and increases the amount of invertase without accelerating its action.

By intermittent exposure of autolyzates for 5 minutes and dialyzates for 2.5 minutes to *ultraviolet rays* and allowing to stand for a time, Gorbach and Ruess⁹ markedly increased the sucrase activity.

V. Euler and Moberg¹⁰ state that *protoplasmic poisons* decrease

¹ Arkiv. Kemi. Mineral. Geol. 1923, **8**, No. 26.

² Z. physiol. Chem. 1919, **106**, 201.

³ Ibid. 1933, **216**, 229.

⁴ J. Biol. Chem. 1930, **87**, 1.

⁵ Enzymologia 1936, **1**, 60.

⁶ Z. physiol. Chem. 1924, **138**, 11, 38.

⁷ Biochem. Z. 1913, **54**, 108, 122.

⁸ J. Biol. Chem. 1921, **48**, 329.

⁹ Biochem. Z. 1934, **271**, 338.

¹⁰ K. Svenska Vetenskapsakademiens Arkiv. Kemi, Miner. Geol. 1918, **7**, No. 12, 1.

the formation of the enzyme, but affect little the action of that already formed. Phosphates and coenzyme are supplemented by another enzyme in alkaline solution.

Anti-invertase.—Preparations of *anti-invertase* of yeast have been shown by Matsuoka¹ to decrease the optical rotation owing to the action of invertase. Heating at 56° C. destroys the rotation-inhibiting action.

Maltase.—Schönfeld and Krumhaar² emphasize the joint action of maltase and zymase in worts, since the greater part of the sugar is maltose. In the antiquated process of growing brewer's yeast on wort, maltase plays an important role. Willstätter, Oppenheimer, and Steibelt³ obtained a very active maltase preparation by extraction of brewer's yeast with water, maintaining neutrality with ammonia.

Leibowitz⁴ demonstrated that yeast and barley maltases are not identical, as shown by the catalyzation of α -methyl and α -ethyl glucoside and the hydrolyzation of β -methyl maltoside by the former, but not by the latter.

Properties.—Notwithstanding the name, maltase is stated by Isaiev⁵ to have a much weaker affinity for *maltose* than for *dextrose*. The hydrolysis of maltose is a reversible reaction, reaching equilibrium at 80 to 85 per cent yield. Dextrose and levulose retard hydrolysis; galactose has no influence. The optimum pH for maltase is 6.1 to 6.7 independent of temperature; the optimum temperature is 30 to 35° C. Activity weakened by short contact with acids or alkalies may be restored. Of the extensive data reported by Willstätter and Baumann,⁶ including results on adsorption by aluminum hydroxide, only the optimum pH, 6.75 to 7.25, is here given.

Amylase.—Maceration juice, an acetone-dried preparation of bottom yeast, containing much maltase but little amylase, according to Gottschalk,⁷ ferments *glycogen*, *erythrocellulose*, *soluble starch*, and *yeast gum* in descending order, the action being intensified by addition of boiled yeast extract (cozymase).

Pringsheim, Borchardt, and Hupfer⁸ present evidence that the

¹ Japan J. Exptl. Med. 1930, 8, 615.

² Wochschr. Brau. 1917, 34, 157, 189.

³ Z. physiol. Chem. 1920, 110, 232.

⁴ Ibid. 1925, 149, 184.

⁵ J. Inst. Brew. 1926, 32, 552.

⁶ Z. physiol. Chem. 1926, 151, 242.

⁷ Ibid. 1926, 153, 215.

⁸ Biochem. Z. 1931, 238, 476.

amylase activator present in autolyzed toluene yeast agrees with *glutathione* in its action.

As determined by Ono,¹ the optima for action on starch are 25 to 30° C. and pH 6.4, and for glycogen 22.5 to 27.5° C. and pH 6.2 to 6.4. Sörensen's phosphate mixture, in 2 per cent addition, acts as activator.

Issoglio² states that Italian law requires that dry yeast have a diastase value of 6500 and yeast extracts 4500 Pollak units as determined by a rapid copper reduction method.

Amylosynthease.—Minagawa³ describes a method of preparing amylosynthease from beer and from compressed and dry yeasts, noting its properties. The dry yeast was found to be rich in amylosynthease originally present in the form of *zymogen*.

Amylopectinase.—Amylopectinase is a name proposed by Nishimura⁴ for an enzyme, similar to maltase, that attacks amylopectin and liquefies starch much faster than amylase. It acts best at pH 6.0 to 6.2 and 20 to 25° C. It is killed at 50 to 60° C.

Inulase.—Gottschalk⁵ identified inulase, also *erythrocellulose*, a minor constituent.

Amygdalase (Emulsin).—Caldwell⁶ brought to notice this enzyme which he showed was different from all other enzymes of yeast.

Bokorny⁷ detected emulsin in compressed brewer's yeast, by the bitter almond odor and the fermentation reaction with yeast and amygdalin, and oil of mustard by the myrosin of yeast acting on potassium myronate. Neither emulsin nor myrosin was destroyed by drying, and both were very resistant to alcohol.

Glucosidase.—Willstätter and Steibelt⁸ classed maltase and α -glucosidase as probably separate enzymes acting in the ratio 7.7 : 0.9.

Helferich, Lampert, and Sparmberg⁹ treat on the dissimilarity of the hydrolysis of α -glucosidase of yeast on glucose, phenol, saligenin, and *o*-cresol and the hydrolysis by β -glucosidase of emulsion on β -glucosides.

¹ J. Agr. Chem. Soc. Japan 1935, **11**, 60, 803; 1936, **12**, 191, 378, 467.

² Industria chimica 1933, **8**, 702.

³ J. Agr. Chem. Soc. Japan 1932, **8**, 508, 811, 1068, 1310; 1935, **11**, 370.

⁴ Bul. Agr. Chem. Soc. Japan 1928, **4**, 126; Biochem. Z. 1930, **223**, 161.

⁵ Z. physiol. Chem. 1926, **153**, 215.

⁶ Proc. Roy. Soc. 1907, **79B**, 350.

⁷ Biochem. Z. 1916, **75**, 376.

⁸ Z. physiol. Chem. 1921, **115**, 199.

⁹ Ber. 1934, **67B**, 1808.

Cellobiase.—*Willia javanica*, according to Groenewege,¹ contains an emulsin that splits amygdalin into dextrose, benzaldehyde, and hydrocyanic acid. He demonstrated that cellobiose cannot be hydrolyzed by emulsin, but by a special enzyme *cellobiase*.

Zymase.—The discovery of this enzyme, of profound significance in fermentation, was accidental. Hans and E. Buchner,² in 1893 found that yeast cells and other minute unicellular forms could be disintegrated by grinding with quartz sand. It was later observed that yeast juice, prepared for medicinal use by hydraulic pressure of the yeast and sand mixture, incited effervescence in sugar added as a preservative. Buchner³ followed up this observation and demonstrated that *yeast juice, acting independently of cellular tissue, causes alcoholic fermentation*.

Buchner's conclusion is now generally accepted, although there are some points in favor of the theory that hydrolytically active protoplasm, which remains active after removal from the cell, causes the changes.

1. Preservation.—Nord and Franke,⁴ by bubbling ethylene gas through freshly prepared yeast juice, prolonged the zymase activity for 65 days by protecting against protease action. The gas also increased the permeability of the cell walls. Kostytshev and Klupt⁵ corroborate the observation of Buchner and others that zymase loses most of its activity on passing through a Chamberland filter, whereas carboxylase, mutase, invertase, and maltase of yeast retain their activity.

2. Action on Carbohydrates.—*Dextrose, levulose, mannose, sucrose, and maltose* ferment readily, *dextrins* and *soluble starch* less readily, *inulin* and cell wall *erythrose* slowly, and *lactose* not at all. *Galactose*, as shown by Harden and Norris,⁶ ferments with juice from specially "trained" yeast. *Glycogen* in the cell, as shown by Harden and Young,⁷ ferments readily; outside the cell, yeast juice acts on it through its diastatic enzyme more rapidly than through its zymase, causing an increase in sugar.

3. Influence of Phosphates.—Phosphorus does not act quantitatively in fermentations where the zymase is formed by the living

¹ Mededeel. Algemeen Proefstation voor den Landbouw. 1921, No. 9, 1.

² Buchner and Hahn: Die Zymasegärung, München, 1903.

³ Ber. 1897, **30**, 117, 1110; 1898, **31**, 568.

⁴ J. Biol. Chem. 1928, **79**, 27.

⁵ Z. physiol. Chem. 1930, **189**, 11.

⁶ Proc. Roy. Soc. London 1910, **82B**, 645.

⁷ J. Chem. Soc. 1902, **81**, 1224.

yeast cells, so it is stated by Elion.¹ When zymase or yeast preparations are added to the substrate, the phosphorus acts quantitatively but not in proportion to the amount. In the presence of *sodium hexose-diphosphate*, highly active zymase maceration juices were secured by Nilsson and Alm² from dry yeast after autolysis and centrifuging; if the autolysis were omitted, the activity was slight. Neuberg and Gottschalk³ brought out that dry top yeast cannot synthesize hexose phosphate, even when coenzyme is added; hence it appears that another zymase constituent is essential.

4. Properties.—Buchner showed that heating at 50° C. destroyed the enzyme, but drying at lower temperatures, addition of common *cellular poisons*, and precipitation and reprecipitation with alcohol and ether did not materially affect the activity. The filtrate through certain types of filter was active, and the same was true of the first portions of the filtrate through the Chamberland filter, but later portions were inactive, owing, as believed by Buchner, to the digestion of the enzyme by protease.

Nilsson and Jansson⁴ determined the ratio of zymase activity to reductase activity by comparing the volume of carbon dioxide evolved per hour with the time required for methylene blue discoloration.

Cozymase.—Buchner and Klatte⁵ studied cozymase, the coenzyme which is essential for the action of zymase. When yeast press juice became inactive, they found that it could be revived by addition of boiled press juice, indicating that the activating substance (coenzyme) contained in the boiled juice replaced the same substance in the active juice that had been used up in fermentation. Although they were convinced that the coenzyme is an organic ester of phosphoric acid, they failed to show that it was one of several phosphoric organic substances examined.

Buchner and Haehn⁶ suggested that cozymase protects zymase from the destructive action of *endotryptase*.

Abderhalden and Schaumann⁷ observed that, by boiling yeast with 10 per cent sulphuric acid and subsequent extraction with alcohol, a solution is obtained that accelerates enzymic action of yeast on *sucrose* and *maltose*, as well as fermentation of dextrose, levulose, and galac-

¹ Nederland. Tijdschr. Hyg., Microbiol. en Serol. 1928, **3**, No. 3, 229.

² Z. physiol. Chem. 1936, **239**, 179.

³ Biochem. Z. 1925, **161**, 244.

⁴ Z. physiol. Chem. 1927, **169**, 73.

⁵ Biochem. Z. 1908, **8**, 520.

⁶ Ibid. 1908, **19**, 191.

⁷ Fermentforschung 1918, **2**, 120.

tose, especially the last, but not *lactose*. Gottschalk¹ showed that the amount of cozymase required for complete fermentation is greater for *glycogen* than for dextrose.

Cozymase occurs also in higher fungi and various green leaves, as shown by micro-fermentation experiments with washed dry yeast, by V. Euler and Steffenburg.²

Vestin, Schlenk, and V. Euler,³ by alkaline hydrolysis of cozymase, obtained diphosphoric acid.

1. Preparation.—V. Euler and Myrbäck⁴ prepared crude cozymase by boiling yeast and filtering. By fractional precipitation of yeast juice with alcohol, between 50 and 80 per cent in a purer form was obtained. They regarded the induction period, varying up to 2 hours of fermentation by dried yeast, as due to “zymophosphate” formation. The essential points in securing optimum action are stated to be pH 6.2 to 6.6, sufficient phosphate, and the proper cozymase : zymase ratio. There is no loss in activity in bubbling air or hydrogen through the solution or in decolorizing.

Myrbäck⁵ regards brewer's yeast as the best source of cozymase, 90 per cent being recoverable. It gives pectose reactions, but is not precipitated by a mixture of copper sulphate and cuprous hydroxide.

2. Chemical Nature.—V. Euler and Nilsson⁶ show that cozymase differs in its action according as it exists free or combined. It can be washed out from dried bottom, but not from dried top yeast. The most active preparation, obtained by V. Euler and Myrbäck,⁷ contained 80 per cent of a *nucleotide*, with a molecular weight of about 450, consisting of *adenine*, *pentose*, and *phosphoric acid*. It is uncertain whether *adenosine nucleotide* is the active constituent or only a carrier of such a constituent. There is also much uncertainty as to the reactions in a solution containing *apozymase* (a complex system from washed dried yeast), *cozymase*, *dextrose*, *hexose diphosphate*, and other phosphates.

Myrbäck, V. Euler, and Hellström⁸ brought out a close relationship of the cozymase of yeast with adenylic acid, corroborating certain results by Dhéré.⁹

¹ Z. physiol. Chem. 1928, **178**, 139.

² Ibid. 1928, **175**, 38.

³ Ber. 1937, **70B**, 1369.

⁴ Z. physiol. Chem. 1923, **131**, 179; 1924, **133**, 260; **136**, 107; **139**, 281.

⁵ Svensk Kem. Tids. 1929, **42**, 3.

⁶ Z. physiol. Chem. 1925, **148**, 23.

⁷ Ibid. 1930, **190**, 93.

⁸ Ibid. 1932, **212**, 7; 1933, **214**, 184.

⁹ Compt. rend. soc. biol. **58**, 34.

Warburg and Christian¹ state that the original Harden-Young coenzyme of fermentation is now known to be composed of three substances: (1) triphosphopyridine nucleotide, the hydrogenating coenzyme of Warburg, (2) diphosphopyridine nucleotide, the cozymase of Euler, and (3) adenine-nucleotide, the phosphorizing coenzyme of Lohmann and Ostern, whose exact chemical nature has not been established.

In experiments by Myrbäck,² cozymase is inactivated in the ratio of 1 : 6 by bone or kidney *phosphatase*, whereas *glycerophosphate* is cleaved in the ratio 1 : 3. The molecular weight is not less than 450. Since the molecular weight of adenylic acid is 347, it is believed that cozymase consists of a compound of adenylic acid and an unknown substance.

Schlenk³ describes cozymase as a hydrogen-donating coenzyme in reversible reaction with dihydrocozymase and consisting of adenine, nicotinic acid, and two molecules each of pentose and phosphoric acid.

3. Coenzyme System.—Lohmann⁴ found that the coenzyme system that forms lactic acid is unlike that of alcoholic fermentation in that the organic constituent is different, but both require the presence of a magnesium salt.

V. Euler, Nilsson, and Jansson⁵ postulate that the oxido-reduction system of washed yeast and muscle differ, since the former utilizes *zymophosphate* and probably *bioglucose*, but not *succinate*, as hydrogen donors, whereas the latter utilizes succinate. The ratio of cozymase and *coreductase* activity in both yeast extract and muscle is 4 : 100, adding further proof of their identity.

Gottschalk⁶ concludes that the intermediate compound in the fermentation of *hexose diphosphate* must be an unknown labile fructose derivative. Robison's *hexose monophosphate* requires for its fermentation more cozymase than Harden and Young's hexose diphosphate.

Cozymase from yeast is stated by V. Euler, Euler, Schlenk, and Günther⁷ to have much less activating power than Warburg's coenzyme from horse blood cells in the dehydrogenation of hexose monophosphate. The cozymase also activates *alcohol-dehydrogenase* of yeast, which the coenzyme does not.

¹ Biochem. Z. 1936, **287**, 291.

² Z. physiol. Chem. 1933, **219**, 173; 1934, **225**, 125.

³ Skand. Arch. Physiol. 1937, **77**, 73.

⁴ Biochem. Z. 1931, **241**, 50, 67.

⁵ Z. physiol. Chem. 1927, **163**, 202.

⁶ Ibid. 1928, **173**, 184.

⁷ Ibid. 1935, **233**, 120.

Galactase.—The galactose-fermenting power secured by culture in galactose-containing medium is attributed by Sohngen and Coolhaas¹ to the formation of a new enzyme.

Glucose.—The enzyme active at 70° C. which Birekner² discovered in beer yeast is not identical with zymase, since it forms neither carbon dioxide nor alcohol, but a carbonlike deposit. It gives a strong pyrrole reaction and acts on dextrose, polyphenols, and lactates.

Phosphatase.—The complicated theories of Schäffner, Bauer, and Berl³ on the role of phosphatases in fermentation are based in part on the assumption that esterification of the phosphoric acid is effected by a specific phosphatase different from yeast phosphatase and that cozymase activates two distinct reactions. Orange seed extract coupled with yeast phosphatase completes the system consisting of *cozymase*, *hexose diphosphate*, and *acetaldehyde*.

Schäffner and Bauer⁴ note that yeast phosphatase attacks α -, not β -*glycerophosphates* and is practically inactive toward *hexose phosphates* and *phosphoglyceric acid*. It differs from animal phosphatases in its high specificity. Bauer, Schäffner, and Krumey⁵ demonstrated that yeast phosphatase hydrolyzes α -*glycerophosphate* several times more rapidly than the β -form and eight times more rapidly than *dihydroxyacetonephosphoric acid*, the preference being most marked during the early stages. Top yeast, according to Albers and Albers,⁶ contains only one phosphatase that acts strongly on both α - and β -*glycerophosphate*. Bottom yeast contains less of this phosphatase and in addition two other forms.

The optimum time for yeast phosphatase, according to Hommerberg,⁷ is one week. Magnesium activates both *glyco*- and *saccharo*-*phosphatase*.

Phosphatase, *aldehyde-mutase (reductase)*, and *methyl glyoxalase* are given by Gottschalk⁸ as being the known components of the *zymase* complex dependent on cozymase for activity in converting *pyruvaldehyde* (methyl glyoxal) into lactic acid.

Two isodynamic phosphatases were identified by Schuchardt⁹ in

¹ J. Bact. 1924, **9**, 131.

² J. Am. Chem. Soc. 1912, **34**, 1213.

³ Z. physiol. Chem. 1935, **232**, 213.

⁴ Ibid. 1935, **232**, 66.

⁵ Ibid. 1935, **237**, 191.

⁶ Ibid. 1935, **235**, 47.

⁷ Svensk Kem. Tids. 1935, **47**, 63.

⁸ Z. physiol. Chem. 1928, **176**, 314.

⁹ Biochem. Z. 1936, **285**, 448.

various yeasts by inactivation with dilute acid or alkali, only the latter form (from brewer's yeast) showing a marked relative specificity.

Hexosediphosphatase.—Harden and MacFarlane¹ state that a solution containing hexosephosphatase may be prepared by autolysis of dried baker's yeast. The optimum acidity, as determined by Kertesz,² is pH 6.5 at 30° C.

Albers and Albers³ identified in top yeast a "hexosediphosphatase" that acts more readily on hexosediphosphate and β -glycerophosphate than on α -glycerophosphate.

Pyrophosphatase.—As obtained by Lüers, Von Zychlinski, and Bengtsson,⁴ the optimum pH of yeast pyrophosphatases is 6.4 to 6.8 and the optimum temperature 42 to 47°. Pyrophosphatase metabolism of the yeast cell is regarded as significant. Bottom yeast pyrophosphatase is active only in the presence of magnesium which is believed by Bauer⁵ to bind the enzyme and substrate.

Saccharophosphatase.—This term is assigned to Djenab and Neuberg⁶ to an enzyme of top and bottom yeast that ferments synthetic sucrosephosphoric acids in neutral, alkaline, and slightly acid solution at 22 to 37° C. Unlike hexose phosphatase, it acts in the living cell.

Warburg's Enzymes.—A *yellow-red oxidizing enzyme*, becoming colorless on reduction, was discovered by Warburg and Christian⁷ in bottom yeast. It does not dialyze through cellophane and is destroyed at 60° C. The reduction is a catalytic process involving a reducing system consisting of Robison's *hexose monophosphate*, a second enzyme, and coenzyme. Molecular oxygen and iron of *pheohemin* of the aerobic cells act as the oxidizing agents, restoring the color. The same enzyme and the reducing system, but not the pheohemin, may be extracted from baker's yeast by Lebedev's method. In the second paper, the discoverers describe methods of preparation.

The third paper is devoted to a *yellow oxidation enzyme*, the active principle of which is a green fluorescent pigment, soluble in water, but much less so in alkali solution. According to the ultimate analysis it has the formula $(C_{13}H_{13}N_4O_2)_n$ or $(C_{12}H_{12}N_4O_2)_n$. Two absorption bands appear at 270 to 350 m μ in the ultraviolet spectrum, an-

¹ Biochem. J. 1930, **23**, 343.

² J. Am. Chem. Soc. 1930, **52**, 4117.

³ Arkiv. Kemi, Min. Geol. 1935, **12B**, No. 3.

⁴ Wochschr. Brau. 1931, **48**, 519, 529.

⁵ Z. physiol. Chem. 1937, **248**, 213.

⁶ Biochem. Z. 1917, **82**, 391.

⁷ Ibid. 1932, **254**, 438; 1933, **257**, 492; **258**, 496; Naturwissenschaften 1932, **20**, 688, 980.

other at 445 $m\mu$, and a continuous fluorescence band from 500 to 630 $m\mu$.

Phytase.—Phytin is stated by Shimoda¹ to serve as nitrogenous food for certain yeasts. It is rendered available by phytase present in the cells. Species of *Saccharomyces* apparently were not included.

Vitamins.—See also Thiamin and Riboflavin above.

Natural yeast is rich in *thiamin* (vitamin B) and *riboflavin* (vitamin G). By irradiation, the *ergosterol* of yeast is converted into a biologically active form (vitamin D). By addition of *carotene* to yeast packed in foil, as practiced and so declared on the label by the Fleischmann Company, vitamin A deficiency is offset. Although the work of Pavcek, Peterson, Elvehjem, Saudek, Colingsworth, and Baldwin² shows that, conditions equal, grain wort yeast is ordinarily higher in vitamin B than molasses-salt or sugar-salt yeast, this deficiency is overcome by regulating the conditions of manufacture or addition of concentrates.

Quantitative chemical results are meager or unsatisfactory for the reason that the vitamins B and G, occurring naturally, until recently have been known only in complexes and it is too early to expect authoritative figures on such components as have been separated. The vitamin contents in terms of units as obtained by biological tests, however, are carefully controlled by the manufacturer.

Hormones.—*Insulin* is here classed as a hormone in conformity to the usage of animal physiologists. There is evidence, however, that it acts as a coenzyme, or as a bios, if indeed this general term survives after the nature and function of the minor constituents of yeast are better understood. The writers advocate chemical rather than biological classification whenever possible.

Brugsch and Horsters³ isolated insulin from yeast, animal organs, beans, and peas. Von Euler and Myrbäck⁴ found that insulin can replace the cozymase of lactic acid bacteria, but not of yeast. Virtanen⁵ explains this failure in the latter case and concludes that muscle, yeast, lactic acid, and propionic acid cozymases are the same. Fürth⁶ found that in the presence of air it does not increase the carbon dioxide evolution by yeast or alter the action on the glycogen.

¹ Centr. Bakt. Parasitenk. 1927, II Abt. 71, 232.

² Wisconsin Agr. Exp. Sta. 1936, Bul. 435, 80.

³ Biochem. Z. 1924, 147, 150.

⁴ Z. physiol. Chem. 1924, 136, 107; Ber. 1924, 57B, 1073.

⁵ Ber. 1925, 58B, 2441.

⁶ Biochem. Z. 1924, 150, 265.

Among the various vegetable products containing a substance that reduces blood sugar similar to insulin, Simola¹ mentions yeast and suggests that it may be a guanidine derivative. An insulinlike substance was extracted by Von Euler² from yeast with 25 per cent alcohol acidified with hydrochloric acid. It reacts in the following system: fresh muscle pulp, methylene blue, dextrose, and phosphate buffer.

Winter and Smith³ bred out insulin from yeast and *B. coli* by cultivating several months in pure cultures. By replacing glucose with lactose in the medium, it was regained by *B. coli*.

Bioses.—See also Hormones above.

The name bios was assigned by Wildiers⁴ to a factor of yeast extract that stimulates fermentation. Lindner⁵ summarizes the discussions of numerous authors on the nature of bios, the fundamental point being the inability of yeast to grow in a solution containing only sugar and mineral matter. MacDonald⁶ secured evidence that yeast synthesizes bios.

Fulmer and Nelson⁷ regarded bios as a complex containing at least two substances promoting yeast growth. Lucas⁸ separated bios I from bios II from malt extract and observed that neither added alone had much influence, but together they greatly stimulated the growth of yeast, although the action varied with the strain.

Eastcott⁹ studied the action of bios I and II, prepared by Lucas's method. Her preparation of bios I was shown to be identical with *inactive inositol*. Stantial¹⁰ added inositol and bios II separately and together to the culture media for 12 species or strains of yeast. Some species did not respond to the addition of inositol; others, including several common strains of baker's and brewer's yeasts, gave greatly increased yields when bios II was supplemented by inositol. She thus substantiated Eastcott's claims. Kögl and Van Hasselt¹¹ state that inactive inositol has never been isolated from yeast, but admit that it

¹ Ann. acad. sci. Fennicae 1927, (A), 29.

² Biochem. Z. 1928, 194, 197.

³ J. Physiol. 1925, 60, v.

⁴ La cellule 1901, 18, 313.

⁵ Deut. Essigindust. 1920, 24, 103; Wochschr. Brauerei 1920, 37, 75.

⁶ J. Biol. Chem. 1923, 56, 489.

⁷ Proc. Iowa Acad. Sci. 1922, 29, 371.

⁸ J. Phys. Chem. 1924, 28, 1180.

⁹ Ibid. 1928, 32, 1094.

¹⁰ Trans. Roy. Soc. Can. 1932, III, 26, 163.

¹¹ Z. physiol. Chem. 1936, 242, 74.

may serve as a part of the bios complex, since under proper conditions it increases the growth of yeast. Janssens¹ separated from egg yolk a lipoid fraction with growth-promoting properties when acting in conjunction with inositol, showing that there are at least two bios factors.

By fractional electrolysis of extracts of yeast, rice bran, malt sprouts, and milk, Williams and Truesdail² separated Wildiers' bios into two fractions, each supplementing the other, but alone almost completely inactive.

Willaman and Olsen³ showed that bios and vitamin B (including G and other fractions) are not identical. Eddy, Kerr, and Williams⁴ obtained, by selective adsorption or precipitation by ferric oxide hydrosol and recovery by removal of the iron with barium hydroxide, orthorhombic crystals ($C_5H_{11}NO_3$), melting at $223^\circ C.$, that functioned like Wildiers' bios. Since they lacked antineuritic power, they were judged not to be vitamin B. Williams, Wilson, and Von der Ahe⁵ isolated bios by the foregoing method in amounts varying according to the strain of yeast and the degree of exhaustion of the medium.

Schultz, Atkin, and Frey,⁶ after demonstrating that thiamin, both natural and synthetic (Merck's Betabion), stimulates fermentation, applied that principle in a fermentation test for vitamin B that showed an average variation of only 14.6 per cent for the rat test. Aminopyrimidine (2-methyl-5-ethoxymethyl-6-aminopyrimidine), another fermentation accelerator, was shown to have a slightly greater activity than thiamin. Further studies by the same authors of the bios action of both substances and of thiazole (4-methyl-5-beta-hydroxyethyl-thiazole) brought out that their action may be as stimulants or inhibitors, depending on whether they act singly or in combination and on the strain of yeast. They also report the discovery of another bios, designated VI, not yet isolated in pure form.

Mineral Constituents.—As shown by the analyses given in the following table, normal yeast ash consists chiefly of 60 to 80 per cent of potassium phosphate and 15 to 20 per cent of magnesium phosphate, other constituents being in small amounts:

¹ Arch. intern. physiol. 1935, **40**, 257.

² J. Am. Chem. Soc. 1931, **53**, 4171.

³ J. Biol. Chem. 1923, **55**, 815.

⁴ J. Am. Chem. Soc. 1924, **46**, 2846.

⁵ Ibid. 1927, **49**, 227.

⁶ Ibid. 1937, **59**, 948, 2457; 1938, **60**, 490.

COMPOSITION OF YEAST ASH

	Ash *	K ₂ O	Na ₂ O	CaO	MgO	Fe ₂ O ₃	P ₂ O ₅	SO ₃	SiO ₂	Cl
	%	%	%	%	%	%	%	%	%	%
Top Yeast:										
Mitscherlich †...	7.7	39.8	...	1.0	6.0	...	53.9	...	tr.	...
Bull †.....	8.9	35.2	0.5	4.5	4.1	0.6	54.7	0.1
Bottom Yeast:										
Mitscherlich †...	7.5	28.3	...	4.3	8.1	...	59.4
Béchamp †.....	...	28.6	1.4	2.4	5.2	5.0	53.7	5.7†
Compressed Yeast:										
Frey §.....	8.7	36.5	0.7	1.4	5.2	tr.	54.5	0.5	1.2	tr.
Dried Yeast:										
Frey §.....	8.7	34.9	1.8	2.8	5.1	0.4	49.4	0.8	0.9	tr.

* In dry yeast. † Mayer: Lehrbuch der Gährungschemie. Heidelberg, 1878, p. 115.

‡ Loss due to acid ash avoided. § Loc. cit. || Carbon 0.8, undetermined 3.1% of ash.

Calcium and sodium salts are stated by Rubinshtein and Burlakova¹ to be unessential for growth, but if present in the nutrient solution both are taken up, the latter in greater amount than the former. Sulphur, present largely in proteins, suffers in ashing a loss which Béchamp avoided by certain precautions; on the other hand, gas flames give off sulphurous fumes readily absorbed by the ash. These and other analytical errors, also variations due to constituents of the medium and conditions of production, deserve consideration in adopting methods and standards. It is doubtful that the Swiss limit of 2.5 per cent of ash in compressed yeast, designed to prevent addition of mineral filler, has been scrutinized in the light of such evidence.

Minor Mineral Constituents. *Iron.*—Ferrous iron is involved in fermentation humin iron catalyzes respiration; iron is an essential component of holozymase (Zuckermandl and Messiner-Klebermass).² Ferric iron acts independent of aeration and causes formation of more yeast but less alcohol than ferrous iron during fermentation (Malkov).³

Aluminum.—A 6 per cent aluminum sulphate solution was shown by Trautwein⁴ to kill bottom yeast and 0.6 per cent to inhibit fermentation. Respiration was much less affected.

Manganese.—See McHargue and Calfee under Copper.

¹ Biochem. Z. 1934, 271, 324.

² Ibid. 1933, 261, 55.

³ Zentr. Bakt. Parasitenk. 1934, II, 91, 161.

⁴ Z. ges. Brauw. 1934, 57, 65, 69.

Copper.—More than 28 mg. per liter of copper salts retards yeast reproduction but less than 14 mg. per kilo may act as a stimulant; yeast takes up minute quantities from wort (Chapman).¹ Copper present in molasses (9.1 to 26.5 mg. per liter) without noticeable influence; addition of carbon counteracts toxicity, but not retardation of growth (Owen and Calma).²

Results by McHargue and Calfee³ show that addition of 10, 7.5, and 10 mg. per kilo respectively of *manganese*, *copper*, and *zinc* as sulphate increased the dry weight of yeast produced. Copper was most effective in stimulating cell division, and all three, especially copper, stimulated carbon dioxide production, anaerobic conditions being most favorable in all cases.

Washed yeast made in copper containers, after second fermentation 0.95 per cent., dry basis (Van Laer).⁴

Zinc.—Baker's yeast 414.86 mg. per kilo, air-dry basis (Birckner).⁵

See also McHargue and Calfee under Copper.

Arsenic.—Lindemann⁶ calls attention to the absorption of arsenic by hops during sulphuring with consequent contamination of wort and yeast.

Iodine.—A process of iodizing yeast has been patented.

Argon.—In the gas evolved in the anaerobic fermentation of 200 grams each of dextrose and moist yeast, after absorption of the carbon dioxide by alkali, Pictet, Scherrer, and Helfer⁷ obtained nitrogen 70.2, oxygen 27.2, and argon 2.6 per cent. Yeast dried *in vacuo* and over sulphuric acid yielded 0.28 to 0.30 cc. of argon per gram.

BAKING POWDER

BAKING POWDER may be defined as non-biological yeast. Certain manufacturers have called it yeast powder. Before the advent of baking powder the housewife had no alternative but to add the active constituents saleratus (sodium bicarbonate, later known as baking soda) and cream of tartar (potassium bitartrate) separately to the dough or batter. To the pharmacist, baking powder is a modification of Seidlitz powder designed for raising the loaf instead of "settling" the stomach. It is a modern convenience, more distinctly American than European. As compared with yeast, it is a time saver, and time in the Western World is money.

It is a food adjunct and not strictly a food, as its function is merely to make the heavy soggy dough-mass light and spongy, thereby

¹ J. Inst. Brew. 1909, **15**, 36.

² Zentr. Bakt. Parasitenk. 1930, **II**, 80, 227.

³ Plant Physiology 1931, **6**, 559.

⁴ Ann. zymol. 1934 [2], **1**, 287.

⁵ J. Biol. Chem. 1919, **38**, 191.

⁶ Wochschr. Brau. 1932, **49**, 257.

⁷ Compt. rend. 1925, **180**, 1629; **181**, 236.

increasing its palatability and digestibility. It is, however, a little more than an adjunct since practically all brands contain a certain percentage of starch, or less often flour, added to improve the keeping power and to standardize the carbon dioxide liberated, which incidentally adds somewhat to the nutritive value.

Sodium Bicarbonate, NaHCO_3 —This alkaline-reacting salt is, with our present knowledge, the only practicable source of carbon dioxide for baking powder now available. It is also sold by every grocery and pharmacy for separate domestic use. Water highly charged with carbon dioxide (plain soda water) or solid carbon dioxide, such as serves for refrigeration, would appear to be well adapted for the purpose, but for various reasons has not been found to meet the requirements. Since the molecular weight of sodium bicarbonate is 84.01, whereas that of sodium carbonate is 106.01, it yields for the same weight nearly 1.262 times as much carbon dioxide and correspondingly less sodium salt residue. Chemically pure dry sodium bicarbonate is more stable than the normal carbonate and is well adapted for use in standardizing acid solutions.

Acid Constituents.—On the farm, the acidity of sour milk has long been utilized to liberate the carbon dioxide from baking soda in biscuit with the advantage of adding to the food value, coupled, however, with the uncertainty of accurately proportioning the acid to carbonate. The same idea scientifically applied is the basis of patents for lactic acid baking powders. Molasses also serves the double purpose of acid and food. Disodium pyrophosphate is a lesser-known acid material said to be used to a limited extent. Theoretically the ideal acid is hydrochloric, since this leaves only common salt as the residue, but the loss of the advantage of ready mixing and the danger of handling a corrosive acid make its use prohibitive in the household and impracticable in the bakery.

Six acid-reacting materials are now in use, namely: (1) cream of tartar (potassium bitartrate), (2) tartaric acid, (3) monocalcium phosphate, (4) disodium pyrophosphate, (5) soda alum (sodium aluminum sulphate), and (6) calcium lactate. Of these only the first five are of importance in the United States.

Cream of Tartar (Potassium Bitartrate), $\text{KHC}_4\text{H}_4\text{O}_6$.—This is the chief constituent of *lees*, or bottom deposit, and *argol*, or side deposit, which separate in the wine vats, after fermentation has well advanced, because of their greater insolubility in the alcoholic liquid. By recrystallization, impurities, especially calcium tartrate, are removed. It acts less rapidly on sodium bicarbonate than tartaric acid,

hence a suitable mixture of the two causes a more prolonged evolution of gas which is regarded as desirable in bread making.

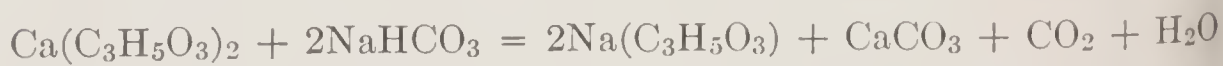
Tartaric Acid, $C_2H_4O_2(COOH)_2$.—Ordinary *d-tartaric acid* ($COOH \cdot HOCH \cdot HCOH \cdot COOH$) is readily prepared from cream of tartar. It differs in its properties from *l-tartaric acid* ($COOH \cdot HCOH \cdot HOCH \cdot COOH$) in that it is dextrorotatory, whereas the latter is levorotatory. Equal portions of the two, as was elucidated by Pasteur in his classical work antedating that on fermentology, constitute *inactive tartaric acid* (*racemic acid*). A fourth form, *meso-tartaric acid* ($COOH \cdot HOCH \cdot HOCH \cdot COOH$), is of scientific interest.

Calcium Monophosphate or Calcium Acid Phosphate, $CaH_4(PO_4)_2$.—This acid salt is today principally made from phosphoric acid derived from distilled elemental phosphorus. It is of remarkable purity and contains less than 2 mg. per kilo of fluorine. As formerly prepared, by treatment of phosphate rock with sulphuric acid, it generally contained several per cent of calcium sulphate, also dicalcium phosphate. In addition to forming the acid constituent of phosphate baking powders, it is employed together with an equivalent amount of sodium bicarbonate in the manufacture of self-rising flour and ready-mixed cake preparations.

Disodium Pyrophosphate or Sodium Acid Pyrophosphate, $Na_2H_2P_2O_7$.—In the last few years the use of this acid salt has greatly increased because of its slow action with sodium bicarbonate.

Anhydrous Soda Alum (Sodium Aluminum Sulphate), $Na_2Al_2(SO_4)_4$.—The corresponding potassium and ammonium double aluminum sulphates (potash and ammonia alums) were formerly used in baking powder, but gave place during the last quarter of the last century to the cheaper sodium salt, following the trend of the times as further evidenced by the substitution of soda lye for potash lye and soda soap for potash soap. Soda alum is known in commerce as S.A.S. It is manufactured from the mineral bauxite.

Calcium Lactate, $Ca(C_3H_5O_3)_2 \cdot 5H_2O$.—This, like alum, is not an acid or acid salt, although classed with them because it liberates carbon dioxide from sodium bicarbonate, the reaction being as follows:



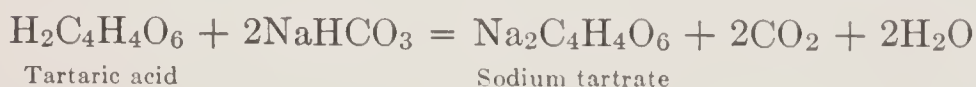
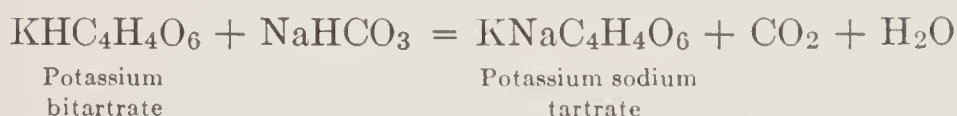
It will be noted that only half of the carbon dioxide is liberated as the gas, hence calcium lactate has not extensive use as a baking chemical. The reaction, as noted by Herrmann and Vogeler,¹ takes place more slowly than with tartaric acid at the same temperature.

¹ Deut. Nähr.-Rundschau 1931, p. 162.

Albumin.—While the addition of a small amount of egg albumin, generally in the proportion of 0.1 per cent, was at one time a common practice, it has now been largely discontinued because it appears to serve no appreciably useful purpose to the consumer. It does, however, give a false appearance of high potential in applying the cold water test, by increasing foam formation. Beaten egg white, as every cook knows, acts as a leavener, and under certain conditions a considerable amount of commercial egg albumin may act in like manner. Jackson ¹ has shown that it has value when the oven heat is low or when the dough stands several hours before baking.

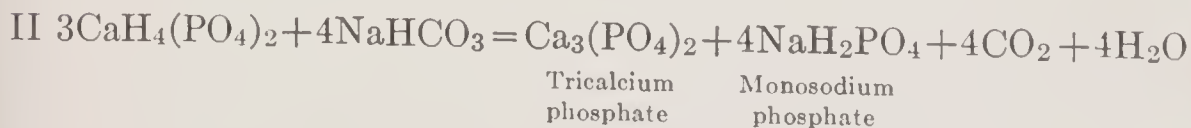
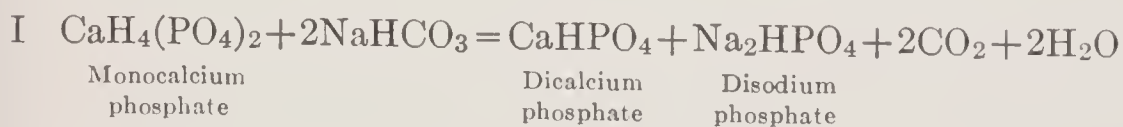
Classification and Reactions of Baking Powders.—Since all modern baking powders contain sodium bicarbonate as the source of carbon dioxide, the classification is based on the acid constituent.

Tartrate Baking Powders.—This type depends for its acidity on cream of tartar with or without a small amount of tartaric acid. The reactions are:



A powder containing 27 per cent of sodium bicarbonate with either 24 per cent of tartaric acid and 49 per cent of starch or with 60 per cent of cream of tartar and 13 per cent of starch yields about 14 per cent of carbon dioxide.

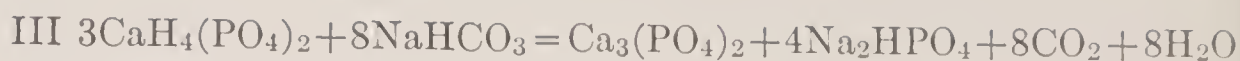
Phosphate Baking Powders.—The acid constituent of this type is monocalcium phosphate of 90 to 95 per cent purity. The equations given below represent three theories of the reactions, I being due to Crampton ² and II and III to Patten: ³



¹ J. Ind. Eng. Chem. 1914, 6, 998.

² U. S. Dept. Agr., Div. Chem. 1889, Bul. 13, Part V, 567.

³ J. Ass. Off. Agr. Chem. 1916, 2, 227.

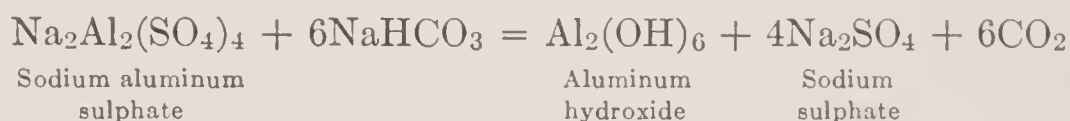


Chittick¹ has proposed an equation which may be regarded as a combination of the equations of Crampton (I) and Patten (III). It is probable that the reaction differs with the conditions, especially the temperature and proportion of ingredients.

A powder containing 27 per cent of sodium bicarbonate, 35 per cent of monocalcium phosphate, and 38 per cent of starch yields about 14 per cent of carbon dioxide.

Pyrophosphate Baking Powders.—In this type of baking powder, disodium pyrophosphate is substituted for monocalcium phosphate, about 10 per cent more of the former being required to equal the same gas production as the latter. The product of the reaction is sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$). Because of its bench tolerance, pyrophosphate baking powder is chiefly used by commercial bakers.

Alum Baking Powders.—At the present time “straight” alum powders are seldom found on the market. The reaction is as follows:



A powder containing 27 per cent of sodium bicarbonate, 27 per cent of anhydrous soda alum, and 46 per cent of starch yields about 14 per cent of carbon dioxide.

Alum Phosphate Baking Powders.—In these the acid constituent is partly calcium monophosphate and partly anhydrous soda alum. Opinions differ as to the reaction.

Crampton² of the U. S. Department of Agriculture gave an equation in which the aluminum passed entirely into the phosphate, one molecule each of monophosphate and alum and four of sodium bicarbonate being involved.

Stokes of the Royal Baking Powder Company later advanced the theory that two reactions take place, one with the phosphate and the other with the alum, and that the aluminum passes largely into the hydroxide. This theory was confirmed in substance by Beans³ of Columbia University, who, however, showed that the alum reaction, taking place in the presence of disodium phosphate formed in the

¹ Graphic Baking Powder Chart: Contribution from the Chemical Laboratory of the Jaques Manufacturing Co., Chicago, Ill.

² Loc. cit.

³ The Reactions of Alum Phosphate Baking Powders, New York, 1926.

phosphate reaction, yields a mixture of aluminum hydroxide with basic aluminum phosphates, a solid solution of aluminum phosphate in aluminum hydroxide, or aluminum hydroxide with absorbed phosphate. In all cases Beans found that the solution filtered from the reaction contained aluminum.

Chittick¹ of the Jaques Manufacturing Company also postulates the formation of both aluminum hydroxide and basic phosphate, but considers that the former varies from zero to an amount always smaller than that of the phosphate. Winton, in the analysis of the water-soluble and insoluble products of a loaf baked with an alum phosphate powder, obtained results at variance with Crampton's equation, but in good agreement with Stokes' theory and fair agreement with Chittick's reaction.

Calcium Lactate Baking Powders.—This type of baking powder has not come into extensive use for reasons stated above.

Legal Rulings. *Alum.*—The physiological aspects of baking powder are beyond the scope of this work; the legal regulation of constituents, however, is of general interest. The alum question has been the subject of bitter controversies. Dr. Wiley and certain medical authorities took a decided stand against the use of alum baking powder, but their contention was not supported by the Referee Board of Consulting Scientists. As a consequence of the Board's report, the sale of alum baking powders is permitted in the United States by federal ruling.

In other countries the laws or rulings are less favorable. According to the latest information available, it is illegal to sell alum baking powder in Australia, Austria, Brazil, Czechoslovakia, Denmark, Dominican Republic, Egypt, France, Germany, Great Britain, Greece, Hungary, Latvia, Mexico, the Netherlands, New Zealand, Newfoundland, Rumania, or Switzerland. In several other countries where the sale of alum baking powders is not specifically prohibited, rulings are in force against the addition to food of alum which by implication includes baking powder.

Monier-Williams² concludes that aluminum should not be allowed in baking powder and self-raising flours, but finds no convincing evidence against aluminum utensils.

Heavy Metals.—Contamination of baking chemicals with undue amounts of lead, arsenic, and other metals, derived from tanks, pipes, etc., was at one time a matter of concern; today, however, such impurities are reduced to a minimum in conformity to legal regulations.

¹ Loc. cit.

² Repts. Publ. Health & Med. Subj. 1935, No. 78.

INDEX

A

Acer saccharum, 36
nigrum, 36
 Acetaldehyde, coffee, 152
 peppermint, 229
 Aceteugenol, bay leaf, 218
 cloves, 298, 299
 Acetic acid, beet molasses, 33
 bergamot, 402
 cane molasses, 22
 caramel, 78
 chicory root, 172
 cloves, 298
 cocoa, 132
 coffee, 147, 148, 152, 153, 158
 Japanese peppermint, 232
 lemon, 405
 maple sand, 42
 sirup, 41
 nutmeg, 353
 orange, 401
 flower, 402
 peppermint, 229
 spearmint, 236
 tea, 103, 104
 water mint, 234
 yeast, 487
 Acetic aldehyde, 491
 Acetic esters, bay leaf, 218
 ginger, 209
 Acetone, caramel, 78
 coffee, 147, 148
 tea, 104
 Acetophenone, 105
 Acetyl, 133
 Acetyl carboxylic acid, 487
 Acetylpropionyl, 152
 Achicoria, 167
 Achroocellulose, 494, 495
 Achroodextrin, 74
 Acids, *see* individual acids
 Ackersenf, 384
 Aconitic acid, 22
 Acore vrai, 191
 Acorin, 195
Acorus Calamus, 191
gramineus, 191

Acquifoliaceæ, 87
 Acrolein, 172
 Adenine, 81-83
 Adenosine triphosphate, 497
 Adenosinetriphosphoric acid, 497
 Adenyl thiopentose, 500
 Adenylic acid, 496
Äerobacter äerogenes, 43
 Ajedrea, 244
 Albahaca, 221
 Albumin in baking powder, 527
 Alecaparra, 283
 Alcaravea, 434
 Alcohol-dehydrogenase, 517
 Alcohols, bay leaf, 218
 nutmeg, 355
Ocimum canum, 224
gratissimum, 224
 spices, 182
 tea, 104
 yeast, 490
 Aldehyde acids, 492
 Aldehyde-mutase, 518
 Aldehydes, *see* individual aldehydes
 Aldehydrase, 510
 Aldoses, 5
 Alhacena, 384
 Alkaloidal products, 81
 constituents, 81
 purine bases, 81
 adenine, 81-83
 caffeine, 81, 82
 formulas, 82
 guanine, 81-83
 tetramethyltrioxypurine, 84
 tetramethyluric acid, 82, 84
 theobromine, 81-83
 theophylline, 82, 84
 pyrimidine bases, 84
 cytosine, 82, 84
 Alkaloids, *see* individual alkaloids
 Allocinnamate, 224
 Alloxazines, xxviii, xxix
 Allspice, 408
 composition, 411
 crown, 408
 Mexican, 408

- Allspice—(*Cont.*)
 oil, volatile, 412
 constituents, 412
 caryophyllene, 412
 cineol, 412
 eugenol, 412
 methyl eugenol, 412
 palmitic acid, 412
 l- α -phellandrene, 412
 values, 412
 pentosans, 413
 standards, 411
 structure, 408
 tannin, 413
 Tobasco, 408
 Allyl cyanide, 370
 isothiocyanate, 369
 sulphide, 182
 thiocyanate, 182
Alpinia, 198
 Allughas, 199
 officinatum, 198
 Alum, in baking powder, 525, 528, 529
 Aluminum, coffee, 162
 tea, 111
 yeast, 523
 Amines, coffee, 147
 yeast, 483
 Amino acids, *see* individual products
 Aminopolypeptidase, 506
 Ammonia, coffee, 148
 Ammonium chloride, 234
Amomis, 408
Amomum angustifolium, 303
 aromatium, 307
 Cardamomum, 303
 Curcuma, 211
 globosum, 303
 Korarima, 303, 307
 maximum, 303
 Mellgueta, 303
 subulatum, 303
 xanthioides, 303
 Amygdalase, 513
 Amyl alcohol, coffee, 156
 peppermint, 229
 yeast, 490
 Amylamine, 483
 Amylase, cellobiogenetic, 43
 honey, 64
 sucrogenetic, 43
 yeast, 512
 Amylodextrin, 74
 starch, 356
 Amylopectinase, 513
 Amylosynthase, 513
 Anasterol, 487
Andropogon citratus, 187
 Nardus, 189
 Sorghum, 25
 saccharatus, 25
 Aneth, 423
 Anethole, 183, 184, 434
 anise, 416, 433, 434
 fennel, 416, 430
 shikimi, 343
 star anise, 343
 structural formula, 184
Anethum graveolens, 423
 sowa, 425
 Aneto, 423
 Anice, 430
 Anis, 430
 estrellado, 341
 étoilé, 341
 Anís, 430
 Anise, 415, 416, 430
 composition, 432
 key, 415
 oil, fixed, 433
 values, 433
 oil, volatile, 433
 constituents, 433
 anethole, 416, 433, 434
 anisealdehyde, 434
 aniseketone, 416, 433, 434
 camphene, 434
 dipentene, 434
 d-fenchone, 434
 methoxybenzylmethylketone, 434
 methyl chavicol, 416, 433, 434
 para-methoxypropyl-benzene, 434
 phellandrene, 434
 α -phellandrene, 434
 d- α -pinene, 434
 standards, 433
 values, 433
 pentosans, 434
 standards, 432
 structure, 431
 Anise, star, *see* Star anise
 Anisealdehyde, 434
 Aniseketone, anise, 416, 433, 434
 fennel, 430
 star anise, 343
 Anthocyanins, coffee, 161
 sugar cane, 23
 Anthophylli, 291

Anthoranthum odoratum, 187, 394
 Anti-invertase, 512
 Apfelsine, 399
 Ápio, 438
 Apiole, 182, 442
 parsley, 416, 442
 Apiols, 442
Apium graveolens, 438
 Petroselinum, 441
 Appio, 438
 Aquaticol, 234
 Araban, 34
l-Arabinose, 133
 Arachidic acid, 157
 Arancio dolce, 399
 Areca, 112
Areca Catechu, 112
 Arecaidine, 112
 Arecaine, 112
 Arecan, 112
 Arecoline, 112
Arenga saccharifera, 28
 Arginine, 32
 Argol, 525
 Argon, 524
 Arsenic, chicory root, 173
 yeast, 524
Artemesia Dracunculus, 255
 Arum family, rhizome spices, 191
 Asarone, 194
 Ascorbic acid, xxii
 cabbage, xxiii
 formula, xxiii
 oranges, xxxi
 paprika, 452
 tea, 105
l-Ascorbic acid, xxii
 Ascorbic acid oxidase, xxiii
 Ascorbigen, xxiii
 Ascosterol, 486
 Asi-rái, 372, 374
 Asparaginase, 506
 Asparagine, 22
Asperula odorata, 394
 Attar of roses, 287
 Aurade, 402
 Azafran, 278

B

Bacillus acidi lacti, 489
 Badiano, 341
 Bagasse, 11

Baies de genièvre, 301
 Baking powder, 465, 524
 acid constituents, 525
 albumin, 527
 classification, 527
 legal rulings, 529
 reactions, 527
 sodium bicarbonate, 465, 525
 Banda mace, 345-347, 351
 nutmeg, 349
 Barbituric acid, 81, 82
 Bark spices, 258
 Barley malt sirup, 75
 Basil, sweet, *see* Sweet basil
 Basilic, 221
 Basilico, 221
 Basiliemünze, 221
 Batavia cassia, 260, 261, 263, 264, 267,
 269, 270
 composition, 264, 269
 structure, 269
 Batavia-Zimt, 269
 Bay leaf, 215
 composition, 217
 oil, volatile, 217
 constituents, 218
 aceteugenol, 218
 acetic esters, 218
 alcohols, 218
 caproic acid, 218
 cineol, 217
 esters, 218
 eucalyptol, 218
 eugenol, 218
 geraniol, 218
 l-linalool, 218
 methyl eugenol, 218
 phenylurethan, 218
 α -pinene, 218
 β -pinene, 218
 sesquiterpenes, 218
 terpenes, 218
 terpineol, 218
 l- α -terpineol, 218
 valeric acid, 218
 values, 217
 pentosans, 218
 structure, 215
 Bay oil, 217, 413
 constituents, 413
 Bayas de enebro, 301
 Bayberry, 408
 Bedstraws, 139
 Beet molasses, *see* Sugar beet products
 sugar, *see* Sugar beet products

- Benzaldehyde, 182
 caramel, 78
 Ceylon cinnamon, 275, 276
 China cassia, 266
 orange flower oil, 402
 orris, 197
 Seychelles cinnamon, 275
 tea, 105
 Benzoic acid, 78, 197, 266, 402
 Benzoylcegonine, 86
 Benzyl alcohol, cloves, 298
 tea, 104, 105
 Benzyl-ethyl alcohol, 104
 Bergamot mint, **231**
 linaloöl, 231
 linalyl acetate esters, 231
 Bergamot oil, **402**
 constituents, 402
 acetic acid, 402
 bisabolene, 402
 camphene, 402
 dihydrocuminic alcohol, 402
 limene, 402
 linalyl acetate, 402
 nerol, 402
 α -pinene, 402
 terpineol, 402
 values, 402
 Betaine, beet molasses, 32
 peppermint, 230
 sugar cane products, 22
 water mint, 234
 Betel nut, **112**
 alkaloids, 112
 arecaidine, 112
 arecaine, 112
 arecoline, 112
 guvacine, 112
 composition, 112
 structure, 112
 Betelnuss, 112
 Betula, 258
Betula lenta, 258
Betulaceæ, 258
 Bioses, 521
 Birch, **258**
 black, 258
 family, bark spices, 258
 oil, 258
 constituents, 259
 methyl salicylate, 259
 standards, 259
 values, 259
 sweet, 258
 Birke, 258
 Bis-5, 7, 3', 4', 5'-pentahydroxyflavopinacol, 107
 Bisabolene, bergamot oil, 402
 lemon, 405
 Bitter fennel, 430
 Black birch, 258
 ginger, 199
 Black mustard, 361, 362, **363**
 carbohydrates, 371
 pentosans, 371
 composition, 367
 enzymes, 370, 371
 myrosin, 370, 371
 myrosinase, 370
 phosphatase, 371
 flour, 367, 371
 mineral constituents, 371
 oil, fixed, 368, 380
 values, 369
 oil, volatile, 369
 allyl cyanide, 370
 allyl isothiocyanate, 369
 carbon disulphide, 370
 sinigrin, 370
 phosphorus-organic compounds, 371
 phytin, 371
 potassium myronate, 370
 proteins, 368
 structure, 363
 Black pepper, **319**, 320
 Acheen, 320, 328-330
 acids, 335
 oxalic, 335
 alkaloids, 331
 chavicine, 333
 hexahydropyridine, 334
 piperidine, 334
 piperine, 319, 331, 332
 Allepy, 320, 329
 carbohydrates, 335
 pentosans, 335
 starch, 335
 sugars, 335
 composition, 327, 330
 decorticated, 329
 diluent, 320
 impurities, 320
 Lampong, 320, 328-330
 Malabar, 328-330
 Mangalore, 320, 328-330
 microscopy, 327
 mineral constituents, 336
 Penang, 329
 proteins, 329
 oil, fixed, 334

- Black pepper—(*Cont.*)
 oil, volatile, 334
 constituents, 335
 caryophyllene, 335
 dipentene, 335
 methylpyrroline, 335
 phellandrene, 335
 piperidine, 335
 values, 334
 shells, composition, 331
 Siam, 329
 Singapore, 320, 328-330
 standards, 329
 structure, 321
 Tellicherry, 320, 329, 330
 Black tea, *see* Tea
 Bockshornklee, 389
 Bohea tea, *see* Tea
 Bohnenkraut, 244
 Bombay mace, 345-348, 351, 352
 Bombilla, 87
Borassus flabellifer, 28
 Borneol, 185
 Ceylon cinnamon, 276
 ginger, 209
 rosemary, 221, 248
 sage, 221, 251
 thyme, 242
 Thymus marschallianus, 243
d-Borneol, cardamom, 307
 nutmeg, 355
l-Borneol, citronella, 190
 coriander, 420
 thyme, 242
 Bornyl acetate, 248
 Boron, cocoa, 136
 coffee, 162
 saffron, 282
 Bouleau, 258
Brassica, 364
 alba, 378
 arvensis, 384
 Besseriana, 363, 372, 374, 375
 campestris, 376
 junceae, 362, 370, 372, 374-377
 lanceolata, 372
 nigra, 362, 363
 oleracea, 438
 ramosa, 377
 Sinapistrum, 384
 Brisbane sassafras, 268
 Brown mustard, 362, 370, 372, 384, 388
 composition, 374
 oil, volatile, 374
 potassium myronate, 370
 Brown mustard—(*Cont.*)
 sinigrin, 370
 structure, 372
 Brown sugar, *see* Sugar cane products
 Butanol, 490
 Butyl alcohol, 490
 Butyraldehyde, 105
 Butyric acid, beet molasses, 33
 honey, 60
 tea, 103, 105
 water mint, 234
 yeast, 487, 489
 Butyrol, 131
- C
- Cacao, 114
 butter, *see* Cocoa butter
 Cacaonin, 134
 Cadinene, cubebs, 340
 grapefruit, 407
 juniper berry, 302
 peppermint, 229
 Thymus marschallianus, 243
 Cadore's key to *Ilex*, 89
 Café, 140
 marron, 140
 Caffé, 140
 Cafféic acid, 159, 160
 Caffeine, alkaloidal products, 81, 82
 cocoa, 128
 coffee, 139, 147-149, 154
 cola nut, 138
 guarana, 113
 madder family, 139
 maté, 91
 tea, 102
 Caffeine-free coffee, 153, 162
 Cafféol, 147, 148, 158
 Caffetannic acid, 147, 153, 159
 Calamene, 194
 Calamenenol, 194
 Calameone, 194
 Calamo, 191
 Calamus, 191
 camphor, 194
 composition, 193
 oil, volatile, 193
 constituents, 194
 acorin, 195
 asarone, 194
 calamene, 194
 calamenenol, 194
 calameone, 194
 calamus camphor, 194
 camphene, 194, 195

- Calamus,
 oil, volatile,
 constituents—(*Cont.*)
 camphor, 194, 195
 eugenol, 194
 n-heptylic acid, 194
 methyl eugenol, 194
 palmitic acid, 194
 pinene, 195
 d- α -pinene, 194
 sesquiterpene, 194
 unsaturated acid, 194
 values, 193
 pentosans, 195
 structure, 191
 Calciferol, xxiv, xxv
 Calcium, China cassia, 267
 cinnamon, 267
 Calcium acid phosphate in baking
 powder, 526
 lactate in baking powder, 526, 529
 malate in maple products, 36
 monophosphate in baking powder,
 526
 Calendula, 282
 mineral constituents, 282
Calendula officinalis, 278
Caltha palustris, 283
Camellia Thea, 94
 Camphene, anise, 434
 bergamot, 402
 calamus, 194, 195
 citronella, 190
 Japanese peppermint, 232
 juniper berry, 302
 nutmeg, 355
 rosemary, 248
 sage, 251
 Seychelles cinnamon, 275
 Thyme, 242
 Thymus marschallianus, 243
d-Camphene, ginger, 209, 210
 nutmeg, 355, 356
 turmeric, 213
l-Camphene, lemon, 405
 orange flower, 402
 Camphor, 260
 calamus, 194, 195
 Ceylon cinnamon, 276
 rosemary, 248
 Seychelles cinnamon, 275
 thyme, 242
d-Camphor, Brisbane sassafras, 268
 cardamom, 307
 Ocimum canum, 224
d-Camphor—(*Cont.*)
 sage, 251
 sassafras, 277
 sweet basil, 223
 turmeric, 213
 Camphylene, 248
 Cane molasses, *see* Sugar cane products
 sirup, *see* Sugar cane products
 Canela, 261, 271
 Batavo, 269
Canella alba, 258
 Canella di Ceylan, 261
Canellacæ, 258
 Canelladi, 269
 Canelle de Batave, 269
 de Ceylan, 271
 de Chine, 261
 Cape saffron, 278
 Caper family, flower spices, 283
 spurge, 283
 Capers, **283**
 composition, 285
 glucosides, 285
 rutin, 285
 mineral constituents, 286
 pentosans, 286
 structure, 283
 substitutes, 283
Capparidacæ, 283
Capparis spinosa, 283
 Cappero, 283
 Câpres, 283
 Capric acid, honey, 60
 orange, 401
 orris, 197
 Caproaldehyde, 105
 Caproic acid, bay leaf, 218
 coffee, 157
 honey, 60
 Japanese peppermint, 232
 lemon, 405
 tea, 103, 105
 Caprylic acid, lemon, 405
 orange, 401
 orris, 197
 tea, 105
 esters, 209
 Capsaicin, capsicums, 460
 cayenne pepper, 459
 paprika, 452
 Capsanthin, 453
Capsicum, 458, 459
 annuum, 443, 449, 453, 455, 459
 grossum, 453
 baccatum, 455, 458

- Capsicum*—(Cont.)
fastigatum, 455
frutescens, 455, 458
minimum, 455
 Capsicums, 443, **459**; *see also* Paprika
 and Cayenne
 African, 452, 461
 American, 459
 Bombay, 455, 459-461
 Bombay cherry, 455, 459-461
 capsaicin, 460
 cherry, 455
 color, 460
 carotene, 460
 lycopene, 460
 lycopersin, 460
 xanthophyl, 460
 composition, 460
 decenovannillylmethylamide, 460
 Japan, 459-461
 Korean, 461
 Louisiana, 459
 Naples, 459
 Niger, 461
 oil, fixed, 460
 South Carolina, 459-461
 South Indian, 459
 Capsorubin, 454
 Capucine, 398
 Caramel, 1, **76**
 acetic acid, 78
 acetone, 78
 caramelan, 76, 77
 caramelen, 76, 77
 caramelin, 76
 commercial, 78
 composition, 76
 dextrin, 77
 formaldehyde, 78
 formic acid, 78
 furfural, 78
 isosaccharosan, 77
 minor constituents, 77
 uses, 76
 Caramelan, 76, 77
 Caramelen, 76, 77
 Caramelin, 76
 Caraway, 415, 416, **434**
 composition, 436
 key, 415
 oil, fixed, 436
 values, 436
 oil, volatile, 437
 constituents, 438
 carveol, 438
 Caraway,
 oil, volatile,
 constituents—(Cont.)
 carvol, 438
 carvone, 416, 438
 d-carvone, 438
 dihydrocarveol, 438
 dihydrocarvone, 438
 limonene, 416
 d-limonene, 438
 values, 437
 pentosans, 438
 standards, 436
 structure, 435
 wild, 437
 Carbohydrates, *see* individual products
 Carboligase, 510
 Carbon disulphide, 370
 Carboxylase, 507
 Cardamom, **303**
 Bengal, 303, 307
 Cameroon, 307
 carbohydrates, 307
 pentosans, 307
 starch, 307
 sugar, 307
 Ceylon, 303, 305-307
 Ceylon-Malabar, 303
 Chinese, 303
 composition, 306
 Java, 303
 Korarima, 307
 long Ceylon, 303, 306, 307
 Madagascar, 303, 305
 Malabar, 303, 306, 307
 mineral constituents, 307
 Mysore, 306
 nutmeg, 303
 oil, volatile, 306
 constituents, 307
 d-borneol, 307
 d-camphor, 307
 cineol, 307
 sabinene, 307
 terpinene, 307
 d- α -terpineol, 307
 terpinyl acetate, 307
 values, 306
 round, 303, 307
 short, 303, 307
 Siam, 303, 306, 307
 standards, 306
 structure, 303
 wild, 303, 306
 Cardamome, 303

- Cardamomo, 303
- Cardamonio, 303
- Carnaubate, 157
- Carnaubic acid, 157
- Carob bean molasses, 75
 - sugar, 75
- Carotene, xix
 - capsicums, 460
 - chillies, 460
 - forage plants, xix
 - honey, 65
 - oranges, xxxi
 - paprika, 454
 - tea, 109
- Carotenoids, coffee, 161
 - tea, 109
- Carthamus tinctorius*, 278
- Carum Carvi*, 434
- Carvacrol, 182, 184, 242
 - Origanum hirtum*, 239
 - majoranoides*, 239
 - virens*, 239
 - savory, 221
 - Summer savory, 245
 - sweet marjoram, 238
 - thyme, 242
 - Thymus capitatus*, 243
 - marschallianus*, 243
 - Winter savory, 246
- Carveol, 438
- Carvi, 434
- Carvol, 438
- Carvone, 185, 438
 - caraway, 416, 438
 - dill, 416, 426
 - spearmint, 221, 236
- d*-Carvone, 438
- dl*-Carvone, 401
- l*-Carvone, 236
- Caryophyllene, 182
 - allspice, 412
 - black pepper, 335
 - Ceylon cinnamon, 275, 276
 - cloves, 299
 - Japanese peppermint, 232
 - rosemary, 248
 - Seychelles cinnamon, 275
- α -Caryophyllene, 298
- β -Caryophyllene, 298
- Caryophyllin, 295
- Caryophyllus aromatica*, 291
- Casease, 126
- Cassia, 260
 - Batavia, *see* Batavia cassia
 - buds, *see* Cassia buds
- Cassia—(*Cont.*)
 - China, *see* China cassia
 - coffee, *see* Coffee cassia
 - Saigon, *see* Saigon cassia
 - wild, 268
- Cassia buds, 263, 264, 357
 - composition, 264, 360
 - pentosans, 360
 - structure, 357
- Cassia affinis*, 163
 - occidentalis*, 163
- Castilloa elastica*, 160
- Catalase, honey, 63, 64
 - tea, 109
 - yeast, 505
- Catechin, 107
- Catechol, 107
- Cayenne pepper, 452, 455
 - adulterants, 457
 - capsaicin, 459
 - color, 459
 - composition, 458
 - microscopy, 457
 - oil, fixed, 459
 - pentosans, 459
 - standards, 458
 - structure, 456
- Cayennepfeffer, 455
- Cedar, oil of, 251
- Céleri, 438
- Celery, 415, 416, 438
 - composition, 439
 - key, 415
 - oil, fixed, 440
 - values, 440
 - oil, volatile, 440
 - constituents, 440
 - limonene, 416
 - d*-limonene, 440
 - palmitic acid, 440
 - phenol, 440
 - sedanolide, 416, 440, 441
 - sedanonic acid anhydride, 440, 441
 - selinene, 441
 - sesquiterpene, 440
 - terpenes, 440
 - values, 440
 - standards, 439
 - structure, 439
- Cellobiase, 514
- Cellobiogenetic amylase, 43
- Cellulose, cocoa, 133
 - coffee, 161
- Cephalin, 497, 498

- Ceratonia Siliqua*, 75
 Cerevisterol, 487
 Cerotic acid, 353
 Ceylon cinnamon, 260, **271**
 composition, 264, 273
 microscopy, 273
 mineral constituents, 267, 268, 276
 calcium, 267
 oil, volatile, 273
 constituents, 275
 benzaldehyde, 275, 276
 borneol, 276
 camphor, 276
 caryophyllene, 275, 276
 cineol, 276
 cinnamal, 275
 cinnamaldehyde, 276
 cuminaldehyde, 275
 cymene, 275
 dipentene, 276
 eugenol, 275, 276
 furfural, 275
 linalool, 276
 l-linalool, 275, 276
 linalyl isobutyrate, 275
 methyl *n*-amylketone, 275
 nonylaldehyde, 275
 phellandrene, 276
 l-phellandrene, 275
 phenyl-propyl aldehyde, 275
 pinene, 276
 l- α -pinene, 275
 safrole, 276
 terpenes, 275, 276
 values, 273, 274
 pentosans, 276
 structure, 272
 Ceylon-Zimt, 271
 Charlock, 362, 366, 367, 372, **384**
 cake, 387
 composition, 387
 oil, fixed, 387
 values, 387, 388
 oil, volatile, 388
 phosphorus-organic compounds, 388
 phytin, 388
 structure, 385
 Chavibetol, 224
Chavica officinarum, 336
 Roxburghii, 337
 Chavicic acid, 332
 Chavicol, 209
 Cherry capsicums, 455
 Chicory root, 142, 150, 151, **167**
 composition, 170, 171
 Chicory root—(Cont.)
 constituents, 171
 acids, 172
 oxalic, 172
 bitter principle, 172
 enzymes, 173
 inulo-coagulase, 172
 inulin, 172
 mineral, 173
 minor mineral, 173
 arsenic, 173
 oil, 171
 acetic acid, 172
 acrolein, 172
 furfural, 172
 furfuryl alcohol, 172
 valeric acid, 172
 Magdeburg, 167, 172
 structure, 167
 Westland, 172
 Chillies, 456, 459; *see also* Cayenne
 pepper
 colors, 460
 carotene, 460
 lycopene, 460
 lycopersin, 460
 xanthophyll, 460
 composition, 458, 460
 decenovannillylmethylamide, 460
 Japan, 458-460
 Louisiana, 459
 Mombassa, 456, 458
 Naples, 459
 Sierra Leone, 456
 Zanzibar, 456, 458
 China cassia, **261-270**
 carbohydrates, 267
 pentosans, 267
 composition, 263, 264
 mineral constituents, 267
 calcium, 267
 oil, fixed, 263
 oil, volatile, 265
 constituents, 265
 benzaldehyde, 266
 benzoic acid, 266
 cinnamal, 266
 cinnamaldehyde, 266
 cinnamic acetate, 267
 cinnamic acid, 267
 cinnamic aldehyde, 266
 cinnamyl, 266
 cinnamyl acetate, 267
 coumarin, 266
 o-methoxycinnamaldehyde, 265

- China cassia,
oil, volatile,
constituents—(*Cont.*)
methyl ortho-coumaraldehyde,
266, 267
methyl salicylaldehyde, 266
phenyl-propyl acetates, 266
salicylaldehyde, 266
salicylic acid, 266
values, 265
standards, 265
standards, 263
structure, 261
- Chinese mustard, **377**
composition, 377
oil, fixed, 377
oil, volatile, 378
structure, 377
- Chitin, 483
- Chloral hydrate, 492
- Chlorogenic acid, 158, 159
- Chlorophyll, 161
- Chocolate, **114**, 124; *see also* Cocoa
adulterants, 127
compounds, 127
milk, 114, 126, 127
sweet, 114, 124, 129
- Cholesterol, xxiii, xxiv, xxv
- Choline, beet molasses, 32
cocoa, 128
coffee, 155
maple sap, 43
sugar cane products, 22
water mint, 234
yeast, 493
- Choline bases, cocoa, 128
coffee, 155
nutmeg, 356
sugar beet products, 32
sugar cane products, 22
yeast, 483
- Chromane, xxvii
- Cichorium Intybus*, 167
- Cicoria, 167
- Cilantro, 416
- Cinchona bark, 139
- Cineol, 185
allspice, 412
bay leaf, 217
cardamom, 307
Ceylon cinnamon, 276
ginger, 209
peppermint, 229
rosemary, 221, 248
- Cineol—(*Cont.*)
sage, 221, 251
spearmint, 236
star anise, 343
sweet basil, 223
tumeric, 213
wild cassia, 268
- Cinnamal, 182, 266
Ceylon cinnamon, 275
China cassia, 266
Seychelles cinnamon, 274, 275
yeast, 492
- Cinnamaldehyde, *see* Cinnamal
- Cinnamic acetate, 267
acid, 267
aldehyde, 266
- Cinnamomo, 271
- Cinnamomum aromatica*, 261
Burmanni, 269, 276
Cassia, 261, 265, 266, 357
glanduliferum, oil, 268
lignea, 267, 268
Loureirii, 270
Massoia, oil, 269
oliveri, oil, 268
parthenoxylon, oil, 269
sintok, oil, 268
vera, 267, 268
zeylanicum, 265, 271
- Cinnamon, 260, 263
Ceylon, *see* Ceylon cinnamon
Madagascar, oil, 274
Mayotta, oil, 275
Padang, oil, 276
Seychelles, *see* Seychelles cinnamon
- Cinnamyl, 266
acetate, 267
- Citral, 185, 405
citronella, 190
ginger, 209
grapefruit, 407
lemon, 405
grass, 188
orange, 401
rose, 289
thyme, 242
- Citral-*a*, 105
- Citraurin, 454
- Citric acid, cane molasses, 22
cocoa, 133
maple sirup, 41
maple sand, 42
- Citrin, xxx
- Citron, 403

- Citronella, **189**
 oil, 189
 constituents, 189
 l-borneol, 190
 camphene, 190
 citral, 190
 citronellal, 189
 citronellol, 190
 citronelloxide, 190
 dipentene, 190
 elenol, 190
 eugenol, 190
 farnesol, 190
 geraniol, 189
 isovaleryl alcohol, 190
 isovalerylaldehyde, 190
 l-limonene, 190
 methyl eugenol, 190
 methyl heptenone, 190
 nerol, 190
 sesquiterpenes, 190
 values, 189
 Citronellal, citronella, 189
 lemon, 405
 Citronelle, 189
 Citronellgras, 189
 Citronellol, citronella, 190
 rose, 288, 289
 tea, 105
 Citronelloxide, 190
 Citropene, 405
Citrus aurantifolia, 406
 Aurantium, 55, 399, 400
 grandis, 407
 sinensis, 399, 400
 bergamia, 402
 decumana, 407
 grandis, 407
 limetta, 406
 Limonia, 403
 Limonium, 403
 Medica, *Limon*, 403
 nobilis, *deliciosa*, 403
 sinensis, 399, 400
 Clary, 219, 221, **252**
 oil, 252
 constituents, 253
 l-linalool, 253, 254
 linalyl acetate, 253
 l-linalyl acetate, 254
 l-nerolidol, 254
 l-nerolidol acetate, 254
 selareol, 221, 253
 sesquiterpene, 254
 values, 252
 Clary—(*Cont.*)
 sage, 252
 wild, 253
 Clavo, 291
 Clove bark, 260
 Cloves, **291**
 Amboyna, 295, 206
 Bencoolen, 296
 composition, 295
 fruit, 291
 Mayotta, 298
 microscopy, 294
 mineral constituents, 299
 mother, 291, 294, 295
 oil, fixed, 295
 caryophyllin, 295
 eugenin, 297
 oil, volatile, 297
 constituents, 298
 acetic acid, 298
 acetoeugenol, 298, 299
 benzyl alcohol, 298
 caryophyllene, 299
 α -caryophyllene, 298
 β -caryophyllene, 298
 dimethyl furfural, 298
 eugenol, 297, 298
 furfural, 298
 furfuryl alcohol, 298
 methyl alcohol, 298
 methyl benzoate, 298
 α -methyl furfural, 298
 methyl-*n*-amyl carbinol, 298
 methyl-*n*-amylketone, 298
 methyl-*n*-heptyl carbinol, 298
 methyl heptylketone, 298
 salicylic acid, 298
 vanillin, 298
 values, 297
 standards, 298
 Penang, 296
 pentosans, 299
 standards, 295
 structure, 291
 tannin, 299
 Zanzibar, 295, 296
 Coca, 85
 family, leaf alkaloidals, 85
 Coca leaf, 85
 composition, 85
 structure, 85
 Cocablätter, 85
 Cocaine, coca leaf, 85
 Cocamine, 86
 Cocarboxylase, 507

- Cocatannic acid, 86
 Coccola di ginepro, 301
 di pimento, 408
 Cochín ginger, 199, 200, 204-206
 Coco, 114
 Cocoa, **114**, 115
 Accra, 119
 African, 120-122
 ammonia process, 128
 Aqua Clara, 120-122
 Ariba Guayaquil, 120-122
 Bahia, 120-122
 Brazilian, 120
 butter, 115, 128, 131
 substitutes, 131
 Caracas, 119-122
 Ceylon, 120-122
 Chuao, 120-122
 composition, 119-127
 effects of fermentation, 126
 of roasting, 120
 germ, 125
 compounds, 127
 constituents, 127
 acids, 132
 acetic, 132
 citric, 133
 oxalic, 132
 pectic, 133
 tartaric, 133
 cacaonin, 134
 carbohydrates, 133
 l-arabinose, 133
 cellulose, 133
 d-galactose, 133
 d-glucose, 133
 lignin, 133
 pentosans, 133
 starch, 133
 xylan, 133
 xylose, 133
 choline, 128
 colors, 133
 cocoa-brown, 134
 cocoa-red, 133
 enzymes, 126
 casease, 126
 diastase, 126
 invertase, 126
 oxidase, 126
 protease, 126
 raffinase, 126
 theobromase, 126
 fat, 128
 composition, 130
- Cocoa,
 constituents,
 fat—(*Cont.*)
 palmitostearoölein, 130
 substitutes, 131
 values, 128
 unsaponifiable matter, 131
 mineral, 135, 136
 minor mineral, 135
 boron, 136
 copper, 136
 iron, 135
 manganese, 136
 oil, volatile, 131
 esters, 132
 hexoic acid, 132
 d-linalool, 132
 n-nonoic acid, 132
 octoic acid, 132
 phosphorus-organic compounds, 135
 lecithin, 135
 proteins, 127
 purine bases, 128
 caffeine, 128
 theobromine, 126, 128
 tannin, 126
 Cuban, 120-122
 Dutch, 115, 120, 124, 128
 germ, 125
 Haiti, 120-122
 Jamaica, 120-122
 La Guayra, 119
 liquors, 133
 Maracaibo, 120-122
 nibs, 119
 Ovello, 120-122
 Puerto Cabello, 119
 San Filipe, 120-122
 San Thomé, 120
 Santa Rosa, 120-122
 shells, 119
 South American, 119, 120
 St. Domingo, 120-122
 structure, 115
 Trinidad, 119-122
 Venezuelan, 119-122
 West Indian, 120
 Cocoa-brown, 134
 Cocoa-red, 133
 Codehydrogenase, 509
 Coenzymes, 505; *see also* Yeast en-
 zymes
 Coffalic acid, 158, 159
 Coffea, 139
 Abeocutæ, 140

Coffea—(Cont.)

- arabica*, 139, 140, 149
- polysperma*, 145
- bengalensis*, 139, 140
- Bonnieri*, 140
- canephora*, 140
- dubardi*, 140
- excelsa*, 140
- liberica*, 139, 140, 149
- Humboltiana*, 140
- Gallieni*, 140
- mauritiana*, 139, 140
- Mogeneti*, 140
- perrieri*, 140
- robusta*, 140
- stenophylla*, 140
- ugandæ*, 140
- Zanguebariæ*, 140
- Coffearine, 155
- Coffee, 139, 140
 - Abeocuta, 140
 - Abyssinian, 141
 - Aden, 141
 - adulterants, 143
 - African, 155
 - Arabian, 139, 141
 - Asiatic, 155
 - Bengal, 140
 - Bogota, 141
 - Café marron, 140
 - caffeine-free, 142, 153, 162
 - Central African, 140
 - Central American, 141, 155
 - Ceylon, 141
 - Chad, 140
 - chicory in, 142
 - Colombian, 141
 - composition, 147-154
 - caffeine-free, 153
 - Defoka, 153
 - extracts, 154
 - influence of roasting, 147
 - of staling, 150
 - of vacuum packing, 150
 - Kaffee Hag, 153
 - Sanka, 153
 - substitutes, 154
 - tannin-free, 153, 154
 - Congo, 140
 - constituents, 154
 - acetaldehyde, 152
 - acetone, 147, 148
 - acetylpropionyl, 152
 - acids, 158
 - acetic, 147, 148, 152, 153, 158

Coffee,

- constituents,
 - acids—(Cont.)
 - caffeic, 159, 160
 - caffetannic, 147, 153, 159
 - carbonic, 147
 - chlorogenic, 158, 159
 - coffalic, 158, 159
 - coffeic, 160
 - formic, 148, 153, 158
 - malic, 159
 - oxalic, 159
 - palmitic, 147, 157
 - quinic, 159, 160
 - valerianic, 158
 - ammonia, 148
 - amyl alcohol, 156
 - caffeol, 147, 148, 158
 - carbohydrates, 160
 - cellulose, 161
 - dextrin, 160
 - galactan, 161
 - galactose, 161
 - hemicellulose, 161
 - mannan, 161
 - mannose, 161
 - pentosans, 161
 - sucrose, 149, 160
 - choline bases, 155
 - choline, 155
 - trigonelline, 155
 - colors, 161
 - anthocyanins, 161
 - carotenoids, 161
 - chlorophyl, 161
 - leucophyl, 161
 - diacetyl, 152, 153
 - diethyl ketone, 153
 - dimethyl sulphide, 150
 - enzymes, 161
 - α -*d*-galactosidase, 161
 - β -*d*-galactosidase, 161
 - α -*d*-mannosidase, 161
 - eugenol, 153
 - furan, 152
 - furfural, 148, 156
 - furfuraldehyde, 152, 153
 - furfuran, 148
 - furfuryl alcohol, 152, 153, 158
 - mercaptan, 152
 - galactan, 161
 - guaiaicol, 152, 153
 - n*-heptacosane, 153
 - hydrogen sulphide, 152
 - hydroquinone, 147

Coffee,

constituents—(*Cont.*)

kahweol, 153, 158

mannan, 161

methyl acetylcarbinol, 153

amine, 147

mercaptan, 152

n-methylpyrrole, 152

mineral, 161

minor mineral, 161

aluminum, 162

boron, 162

copper, 162

fluorine, 162

iodine, 162

iron, 161

oil, fixed, 156

arachidic acid, 157

caproic acid, 157

carnaubic acid, 157

composition, 157

daturic acid, 157

kahweol, 158

linolic acid, 157

myristic acid, 157

oleic acid, 157

palmitic acid, 157

stearic acid, 157

tannol carnaubate, 157

tetracosane, 157

values, 156

wax, 157

oil, volatile, 158

acetic acid, 158

caffeoil, 158

furfuralcohol, 158

phenols, 158

valerianic acid, 158

phenols, 158

potassium caffeine chlorogenate,
160

purine bases, 154

caffeine, 139, 147-149, 154

coffearine, 155

pyrazine, 152

pyridine, 152, 155

pyrrol, 147, 155

resorcin, 148

sulphur compounds, 153

sylvestrene, 153

tannol carnaubate, 157

terpenes, 153

trimethylamine, 148

vanillone, 153

p-vinyl catechol, 153

Coffee,

constituents—(*Cont.*)

vinyl guaiacol, 152

p-vinyl guaiacol, 153

wax, 157

decortication, 141

dry process, 141

wet process, 141

Defoka, 142, 153

East African, 140, 141

East Indian, 140, 141, 149

Ecuador, 141

Equatorial Africa, 140

extracts, 142, 154

German colonies, 154

grinding, 141

Guiana, 141

Haiti, 141

Indian, 140, 141

Indo-china, 140

Jamaican, 141

Java, 139, 141, 149, 151, 161

Kaffee Hag, 142, 153

Liberian, 139

long berry Mocha, 141

Madagascan, 140

Maracaibo, 141, 161

Mascarene Islands, 140

Menado, 145

Mexico, 141

Mocha, 141, 149-151, 161

Nigeria, 140

Portuguese, 154

Puerto Rico, 141, 150, 151

Quillu, 140

Rio, 141, 150, 151, 161

roasting, 141

Robusta, 140

Sanka, 142, 153

Santo Domingo, 141

Santos, 141, 150, 151, 155

São Paulo, 141

short berry Mocha, 141

Sierra Leone, 140

Snoussi, 140

South American, 155

staling, 150

substitutes, 142, 150, 154, 163

Sumatra, 141

structure, 144

tannin-free, 142, 153, 154

Uganda, 140

vacuum-packed, 142, 150

varieties, 145

Venzuelan, 141

- Coffee—(*Cont.*)
 West African, 139-141
 West Indian, 141
 wild, 140, 155
 Yemen, 141
 Zanzibar, 140
- Coffee cassia, **163**
 composition, 165
 oil, 166
 structure, 163
- Coffeic acid, 160
- Cola, 137
acuminata, 137
nitida, 137
vera, 137
- Cola nut, **137**
 alkaloids, 138
 composition, 138
 glucosides, 138
 purine bases, 138
 caffeine, 138
 theobromine, 138
 structure, 137
- Colors, *see* individual products
- Comino, 420
 di Malta, 420
- Compositæ*, 167, 253
- Composite family, chicory root, 167
 dandelion root, 173
 honey, 52, 54
 leaf spice, 253
- Conalbumin, xxxiii
- Coniferin, 42
- Copper, cocoa, 136
 coffee, 162
 fenugreek, 393
 honey, 66
 molasses, 24
 yeast, 524
- Coproporphyrin, 503
- Coreductase, 508
- Coriander, 415, **416**
 composition, 417
 key, 415
 oil, fixed, 418
 values, 418
 oil, volatile, 418
 constituents, 419
 l-borneol, 420
 coriandrol, 416, 419, 420
 cymene, 419
 2-decen-1-aldehyde, 420
 n-decylc aldehyde, 420
 dipentene, 419
 geraniol, 420
- Coriander,
 oil, volatile,
 constituents—(*Cont.*)
 d-linalool, 419, 420
 8-methyl-2-nonen-1-aldehyde,
 420
 phellandrene, 419
 β -pinene, 419
 d- α -pinene, 419
 dl- α -pinene, 419
 α -terpinene, 419
 γ -terpinene, 419
 terpinolene, 420
 values, 419
 pentosans, 420
 standards, 418
 structure, 416
- Corianderlo, 416
- Coriandrol, 416, 419, 420
- Coriandrum sativum*, 416
- Corn glucose, 73, 74
 Indian, sugar, 2
 malt sirup, 75
 stalk products, 27
- Corypha cerifera*, 143
- Cosettes, 29
- Coumarane, xxvii
- Coumarin, China cassia, 266
 tonka bean, 394, 396
 vanilla substitutes, 309
- Coumarouna odorata*, 394
oppositifolia, 394
- Coussarea hydrangeæfolia*, 90
- Cozymase, 515
- Cream of tartar, 525
- Cresol, 104, 105
- Crocetin, 282
- Crocin, 282
- Crocus sativus*, 278
vernus, 278
- Crotonyl mustard oil, 370
- Crown allspice, 408
- Cruciferae*, 361
- Cryptosterol, 486, 487
- Cryptoxanthin, 454
- Cubeb camphor, 340
- Cubeba, 339
- Cubeba officinalis*, 339
- Cubebe, 339
- Cubebic acid, 340
- Cubebin, 340
- Cubebs, 319, **339**
 composition, 340
 cubebic acid, 340

Cubebs—(Cont.)

- oil, fixed, 340
- cubebin, 319, 340
- oil, volatile, 340
- constituents, 340
- cadinene, 340
- cubeb camphor, 340
- dipentene, 340
- pinene, 340
- values, 340
- structure, 340

Cuca, 85

Cumin, 415, 416, 420

- composition, 421
- key, 415
- oil, fixed, 422
- values, 422
- oil, volatile, 422
- constituents, 423
- cumin aldehyde, 423
- cuminal, 416, 423
- cuminic acid, 423
- cymene, 423
- hydrocuminene, 423
- values, 422
- standards, 421
- structure, 420

Cuminal, 182

- cumin, 416, 423

Cuminaldehyde, Ceylon cinnamon, 275

- cumin, 423

Cuminic acid, 423

Cuminum Cyminum, 420

Cumo-tocopherol, xxvii

l-Curcumene, 213

Curcumin, 198

- turmeric, 214

Curcumone, 213

Curcuma, 211

Curcuma, 198, 211

- amada*, 211
- aromatica*, 198, 211, 213
- domestica*, 213
- longa*, 198, 211
- rotunda*, 211
- Zedoaria*, 198, 211

Cyclic aldehyde, 492

Cymbopogon citratus, 187

- flexuosus*, 187
- Nardus*, 189
- Winterianus*, 189

Cymene, 182, 184

- Ceylon cinnamon, 275
- coriander, 419

Cymene—(Cont.)

- cumin, 423
- fennel, 430
- ginger, 209
- Seychelles cinnamon, 275
- Summer Savory, 246
- p*-Cymene, nutmeg, 355
- star anise, 343
- Thymus marschallianus*, 243
- Cymol, *Origanum hirtum*, 239
- Smyrneum*, 239
- Summer savory, 246
- thyme, 242
- p*-Cymol, 343
- Cynnamlcocaine, 86
- Cytochrome, 503
- Cytosine, 81, 82, 84

D

Dalbergia, 394

Dandelion root, 173

- composition, 174
- inulin, 174
- laevulin, 174
- structure, 173

Date palm sugar, 28

Daturic acid, 157

Decaldehyde, 492

2-Decen-1-aldehyde, 420

Decenovannillylmethylamide, capicums, 460

- chillies, 460

Decyl alcohol, 401

- aldehyde, grapefruit, 407
- orange, 401
- flower oil, 402

n-Decylaldehyde, coriander, 420

- lemon grass, 188
- orris, 197

Decylic acid, 197

- aldehyde, 209, 210

Defoka, 142, 153

Dehydrase, 508

7-Dehydrocholesterol, xxiv

22-Dehydroergosterol, xxv

Dehydrogenase, alcohol, 509

- glutamic acid, 508
- lactic acid, 508
- yeast, 508

Dent-de-lion, 173

Depside, 159

Dextran, 494

Dextrin, 1, 46

- caramel, 77

- Dextrin—(*Cont.*)
 coffee, 160
 commercial, 74
 honey, 62
 Dextrose, (*d*-glucose), 1-3, 5, 6, 9, 23
 nectar, 46
 peppermint, 230
 sugar cane products, 23
 water mint, 234
 Diacetyl, 152, 153
 Dialdehydes, 492
 Diastase, cocoa, 126
 honey, 63
 tea, 109
Dicypellium caryophyllatum, 260
 Diente de león, 173
 Diethyl ketone, 153
 Dihydrocuminic alcohol, bergamot, 402
 spearmint, 236
 α -Dihydrosterol, 487
 Dihydrocarveol, caraway, 438
 spearmint, 231, 236
 Dihydrocarvone, 438
 Dihydrothiochrome, 602
 Dihydroxystyrene, 160
 Dill, 415, 416, 423
 apiole, 436
 composition, 424
 key, 415
 oil, fixed, 425
 values, 425
 oil, volatile, 425
 constituents, 426
 carvone, 416, 426
 dill apiole, 426
 isomyristicin, 426
d-limonene, 426
 myristicin, 426
 phellandrene, 426
 terpinene, 426
 values, 425
 standards, 424
 structure, 423
 Dille, 423
 6,7-Dimethyl-arabityl-alloxazine, xxix
 Dimethyl furfural, 298
 6,7-Dimethyl-rhamnityl-alloxazine, xxix
 6,7-Dimethyl-9-[*d*, 1'-ribityl]-alloxazine, xxviii
 Dimethyl sulphide, 182
Brassica juncea, 370
 coffee, 150
 peppermint, 229
 1,3-Dimethylxanthine, 84
 6,7-Dimethyl-xylityl-alloxazine, xxviii
 Dipentene, anise, 434
 black pepper, 335
 Ceylon cinnamon, 276
 citronella, 190
 coriander, 419
 cubebs, 340
 fennel, 430
 lemon, 405
 grass, 188
 mace, 354
 nutmeg, 355, 356
 orange flower, 402
 sage, 251
 spearmint, 236
 star anise, 343
 Summer savory, 246
 Dipeptidase, 506
Dipteryx odorata, 394
 Disodium pyrophosphate in baking powder, 526
 Dotriacontane, 234
 Duodecylic acid, 197
- E
- Ecgonine, 86
 Elenol, 190
Elettaria Cardamomum, 303
Embelia ribes, 320
 Emulsin, saffron, 282
 yeast, 513
 Endotryptase, 507, 515
 Eneldo, 423
 Enzymes, *see* individual products
l-Epicatechol, 107
 Episterol, 487
 Erepsin, 506
 Ereptase, 505
 Ergadenylic acid, 497
 Ergosterol, xxv
 yeast, 485, 487
Eriophyes thomasi, 238
 Erythrocellulose, 494, 495, 513
 Erythrodextrin, 74
Erythroxylacæ, 85
Erythroxylon Coca, 85
 Esters, *see* individual products
 Estragol, 224
 Estragon, 255
 Ethanol, 490
 Ether extract, spices, 183
 Ethyl aldehyde, 491
 alcohol, 490

Ethylamylcarbinol, 232
 Etioporphyrin, 504
 Eucalyptol, *Ocimum canum*, 224
 Saigon cassia, 271
Eucalyptus globulus, 55
Eugenia, 409
 aromatica, 291
 caryophyllata, 291
 Pimenta, 408
 Tobasco, 408
 Eugenol, 184, 298
 allspice, 412
 bay leaf, 218
 calamus, 194
 Ceylon cinnamon, 275, 276
 citronella, 190
 cloves, 297, 298
 coffee, 153
 nutmeg, 355
 Ocimum gratissimum, 224
 sanctum, 224
 Papua Massoi oil, 269
 Saigon cassia, 271
 sassafras, 277
 Seychelles cinnamon, 274, 275
 wild cassia, 268
 Eugenyl methyl ether, 268
 Euginin, 297
Euphorbia, 46, 47
 lathyris, 283
 Extracts, 177; *see also* Spices

F

Family, arum, 191
 birch, 258
 caper, 283
 coca, 85
 composite, 167, 253
 ginger, 198
 grass, 187
 holly, 87
 iris, 196, 278
 laurel, 215, 260, 357
 madder, 139
 magnolia, 341
 mint, 219
 mustard, 361
 myrtle, 291, 408
 nasturtium, 398
 nightshade, 443
 nutmeg, 345
 orchid, 308
 palm, 112

Family—(Cont.)

parsley, 414
 pea, 163, 389
 pepper, 319, 389
 pine, 301
 rose, 287
 rue, 399
 soapberry, 113
 sterculia, 114
 tea, 94
 violet, 290
 Farnesol, citronella, 190
 lemon grass, 188
 orange flower, 402
 rose, 289
 Fat; *see* individual products
 Fecosterol, 486
 Fedegoso, 163
 Fenchel, 426
 Fenchone, 416, 430
d-Fenchone, 434
 Fennel, 415, 416, 426
 bitter, 430
 composition, 428
 key, 415
 oil, fixed, 429
 values, 429
 oil, volatile, 429
 constituents, 430
 anethole, 416, 430
 aniseketone, 430
 cymene, 430
 dipentene, 430
 fenchone, 416, 430
 limonene, 416, 430
 methyl chavicol, 430
 α -phellandrene, 430
 d-pinene, 430
 values, 429
 pentosans, 430
 standards, 429
 structure, 427
 sweet, 429
 Fenogreco, 389
 Fenouil, 426
 Fénugrec, 389
 Fenugreek, 389
 carbohydrates, 391, 393
 mucilage, 393
 composition, 391
 enzymes, 393
 seminase, 393
 fat, 392
 values, 392
 flour, 393

Fenugreek—(*Cont.*)
 mineral constituents, 393
 minor mineral constituents, 393
 copper, 393
 manganese, 393
 oil, volatile, 393
 phosphorus-organic compounds, 393
 lecithin, 393
 nucleoalbumin, 393
 phospholipins, 303
 phytin, 393
 proteins, 391
 α -albumin, 392
 β -albumin, 392
 globulin, 391
 nucleoprotein, 392
 prolamin, 392
 structure, 389
 Fermentation, 470
 factors, 471
 mediums, 479
 constituents, 479; *see also* Yeast
 theory of Harden and Young, 473
 of Gay-Lussac, 471
 of Kostytshev, 473
 of Lebedev, 475
 of Meyerhof, 475
 of Neuberg, 472
 of Palladin and Sabinin, 473
 of Schade, 473
 Fermenting mediums for yeast, 479
 constituents, *see* Yeast
 Feuille de coca, 85
 de laurier, 215
 Fève tonka, 394
Ficus elastica, 160
 Finocchio, 426
 Fiori del cinnamone del Malabar,
 357
 Flavin, 501
 Flavone, xxx
 Flavanol glucoside, xxx
 Flavoring principles of spices, 183
 Fleurs de cannellier, 357
 Florence fennel, 426, 427
 Flores de cassia, 357
 Flower spices, 278
 Flower bud spices, 291
 Flower-de-luce, 196
 Fluorine, coffee, 162
 tea, 111
Fœniculum officinale, 426
 panmorium, 429
 piperitum, 430
 vulgare, 426

Formaldehyde, caramel, 78
 orange, 401
 yeast, 492
 Formic acid, beet molasses, 33
 cane products, 22
 caramel, 78
 coffee, 148, 153, 158
 honey, 60
 Japanese peppermint, 232
 maple sand, 42
 sirup, 41
 nutmeg, 353
 orange, 401
 yeast, 487
 water mint, 234
 Fructose, 2
 β -*d*-Fructose, 6, 7
d-Fructose, 5, 6
l-Fructose, 5
 Fruit spices, 301
 Fumaric acid, maple sand, 42
 maple sirup, 41
 Furan, 152
 Furfural, caramel, 78
 Ceylon cinnamon, 275
 cloves, 298
 coffee, 148, 156
 Japanese peppermint, 230
 orris, 197
 Furfuraldehyde, 152, 153
 Furfuran, 148
 Furfurol, 172
 Furfuryl alcohol, chicory, 172
 cloves, 298
 coffee, 152, 153, 158
 mercaptan, 152
 Fuscazinic acid, 34

G

Galactan, 161
 Galactase, 518
 Galactose, 161
d-Galactose, 133
 α -*d*-Galactosidase, 161
 β -*d*-Galactosidase, 161
 Galangal, 198
 Galium, 139
 Gallocatechol, 107
 Gallotannase, 107
 3-Galloyl-*l*-acacatechin tannase, 108
 Garofano, 291
Gaultheria, 258
 fragrantissima, oil, 259
 punctata, oil, 259

- Gelbwurz, 211
 Genigbre, 198
 Gentiobiose, 492
 Geranial, 405
 Geraniol, 185
 bay leaf, 218
 citronella, 189
 coriander, 420
 grapefruit, 407
 lemon grass, 188
 nutmeg, 355
 Ocinum canum, 224
 orange flower, 402
 rose, 288, 289
 tea, 104, 105
 thyme, 242
 Geranyl acetate, 405
 Gewürznelken, 291
 Gingembre, 198
 Ginger, 198
 African, 199, 204-206
 ale, 199
 Asia, 198
 Bengal, 205
 black, 199
 Calcutta, 199, 204-206
 Calicut, 206
 carbohydrates, 210
 China, 198, 199
 Cochin, 199, 200, 204-206
 composition, 203
 East Indian, 199
 Indian, 199
 Jamaica, 199, 200, 204-206, 210
 Japan, 198-200, 204-206
 mango, 211
 microscopy, 203
 oil, fixed, 207
 gingerol, 207
 heptylaldehyde, 208
 shogaol, 208
 zingerone, 207
 zingiberone, 207
 oil, volatile, 208
 constituents, 209
 acetic esters, 209
 borneol, 209
 d-camphene, 209, 210
 caprylic esters, 209
 chavicol, 209
 cineol, 209
 citril, 209
 cymene, 209
 decylic aldehyde, 209, 210
 heptyl aldehyde, 209
 Ginger,
 oil, volatile,
 constituents—(*Cont.*)
 isozingiberene, 210
 linalool, 209
 methyl heptenone, 209
 nonylaldehyde, 209
 α -phellandrene, 210
 β -phellandrene, 209
 zingiberene, 209, 210
 zingiberol, 209, 210
 values, 209
 pentosans, 210
 Philippine, 209
 proteins, 207
 Seychelles, 209
 Siam, 199
 Sierra Leone, 199
 standards, 206
 structure, 199
 Ginger family, 198, 303
 fruit spices, 303
 Gingerol, 207
 Girofles, 291
 Globulin, fenugreek, 391
 rape, 380
 white mustard, 380
 Glucose, 518
 Glucose, 72
 commercial, 73
 composition, 73
 corn, 73, 74
 dextrin, 74
 maize, 74
 manufacture, 72
 potato, 73, 74
 standards, 72
 uses, 73
 sirup, 47
 α -*D*-Glucose, 6, 7
 D-Glucose, 5; *see also* Dextrose
 cocoa, 133
 β -*D*-Glucose, 7
 L-Glucose, 5
 Glucosidase, 513
 Glucosides, *see* individual products
 Glucovanillic alcohol, 317
 Glucovanillin, 317
 L-Glutamic acid, sugar beet products,
 32
 Glutamine, 22
 Glutathione, legumes, xxiii
 yeast, 500
 Glutose, 23

Glycerol, peppermint, 230
 yeast, 491
 Glycocoll, 21
 Glycogen, 492
 Glycophosphatase, 518
 Gossypose, *see* Raffinose
 Grains of paradise, 207, 303
Gramineæ, 187
 Grapefruit, 407

oil, 407
 constituents, 407
 cadinene, 407
 citral, 407
 decyl aldehyde, 407
 geraniol, 407
 limonene, 407
 methyl anthranilate, 407
 octyl alcohol, 407
 octyl aldehyde, 407
 sesquiterpenes, 407
 wax, 407
 values, 407

Grapevine sirup, 75
 Grass family, leaf spices, 187
 Grasse sweet basil, 223
 Guaiacol, coffee, 152, 153
 maple products, 42
 Guanine, alkaloidal products, 81-83
 sugar cane products, 22
 tea, 103
 Guarana, 113
 composition, 113
 structure, 113
 Gums, 46
 Guvacine, 112

H

Haba tonca, 394
 Hadromal, 42
 Harden acid, 496
 Harden and Young ester, 474, 495,
 517
 Heliotropin, 182, 317
 vanilla, 318
Helix pomatia, 492
 Hematin, 502
 Hematoporphyrin, 503
 Hemicellulose, coffee, 161
 yeast, 494
 Hemin, 502, 504
 Hemochromogen, 502
 Hemoglobin, 503
n-Heptacosane, 153

Heptoic acid, 103
 Heptyl aldehyde, 208, 209
 Heptylic acid, 234
n-Heptylic acid, 194
 Herbe puante, 163
 Hesperidin, 230
 Hesperetin, 230
 Hexadecenoic acid, 103
 Hexanal, 105
 α , β -Hexanal, 104, 105
 3-Hexen-1-ol, 104
 α , β -Hexenic acid, 232
 Hexenoic acid, 105
 Hexenol, 105
 β , γ -Hexenol, Japanese peppermint,
 232
 tea, 104, 105
 Hexoic acid, chicory, 132
 tea, 104
 Hexose diphosphate, 495
 Hexose monophosphate, 495, 496
 Hexosediphosphatase, 519
 Hexosediphosphoric acid, 495
 Hexosemonophosphoric acid, 496
n-Hexyl alcohol, 104
 Hexylic acid, 234
 Hinojo, 426
 Histidine, 32
 Holly family, leaf alkaloids, 87
 Honey, 45
 adulteration, 47
 alder, white, 54, 55
 alfalfa, 52, 53, 55, 59
 algarroba, 54-56, 59, 63
 alsike clover, 53, 55
Anacardiaceæ, 54
 apple, 53, 55
 arrow weed, 54, 55
 artificial, 68
 aster, wild, 54, 55
 basswood, 52, 54, 59, 63
 blue gum, 55
 blueberry, 61
 buckwheat, 51-53, 55, 66
 wild, 53, 55
 cabbage palm, 53, 55
Cactaceæ, 55
 cat claw, 53, 55
 clover, alsike, 53, 55
 red, 51
 sweet, 53, 55
 white, 51, 53, 55
Campositæ, 52, 54
 composition, 52-58
 American, 53-55, 59, 64

Honey,

composition—(*Cont.*)

- Argentine, 58
- California, 64
- Cuban, 56, 57
- Dutch, 56, 57
- French, 56, 57
- Haitian, 56, 57
- Hawaiian, 46, 53-56, 58, 59, 62, 63
- honeydew, 52, 55, 56, 62, 65, 66
- Hungarian, 58
- Greek, 56, 57, 59, 61
- influence of age, 58
- Italian, 58, 59
- Mexican, 56, 57

constituents, 58

- acids, 60
 - hydrogen ion concentration, 60
- carbohydrates, 60
 - dextrin, 62
 - invert sugar, 60
 - maltose, 62
 - melezitose, 62
 - pentosans, 63
 - sucrose, 61

carotene, 65

colloids, 59

colors, 65

enzymes, 63

- amylase, 64
- catalase, 63, 64
- diastase, 63
- inulase, 63
- invertase, 63
- oxidase, 63, 64
- protease, 63, 64
- peroxidase, 63, 64
- reductase, 63, 64

flavor, 65

fluorescence, 65

methyl anthranilate, 65

mineral, 65

minor mineral, 66

copper, 66

iron, 66

manganese, 66

proteins, 58

tannin, 59

Cornaceæ, 54

cotton, 54, 55

cranberry, mountain, 61

Cucurbitaceæ, 54

dandelion, 54, 55

Ericaceæ, 54*Fagaceæ*, 53Honey—(*Cont.*)

fermentation, 47

floral, 45

formation, 45

golden-rod, 54, 55

grape, 65

gum, blue, 55

heartsease, 53, 55

hickory, 52, 53, 55, 59, 63

honeydew, 46, 51, 52, 55, 56, 60, 62, 65, 66

hop vine, 52, 53, 55

Juglandaceæ, 53

laurel, 54, 55

Leguminosæ, 52-54

locust, 53, 55

Magnoliaceæ, 53*Malvaceæ*, 54

mangrove, 52, 54, 55

melon, 54, 55

Menthaceæ, 54

mesquite, 54, 55

Moraceæ, 53

mountain cranberry, 61

Myrtaceæ, 54, 55

noors, 46

oak, 52

white, 53, 55, 59, 63

ohia lehua, 55, 56

orange, 54, 55, 65, 66

palm, cabbage, 53, 55

palmetto, saw, 53, 55

palmetto-berry dew, 53

pear, prickly, 55

pennyroyal, wild, 54, 55

Phænicaceæ, 53

physical characters, 49

color, 51

flavor, 49

granulation, 51

polarization, 51

pollen, 48, 50

histology, 49

Polygonaceæ, 53

poplar, 52, 53, 55, 59, 63

prickly pear, 55

raspberry, 53, 55

red, 53, 55

wild red, 53, 55

red clover, 51

raspberry, 53

Rosaceæ, 52, 53*Rutaceæ*, 54

sage, 51, 52, 54, 55

Salicaceæ, 53

Honey—(Cont.)

- saw palmetto, 53, 55
- Spanish needle, 54, 55
- Stachys*, 58
- standards, 45
- structure, 48
 - pollen, 47-50
- sumac, 52, 54, 55
- sweet clover, 53, 55
- Tiliaceæ*, 54
- Titi, 66
- tupelo, 51, 52, 54, 55
- white alder, 54, 55
 - clover, 51, 53, 55
 - oak, 53, 55, 59
- whitewood, 53, 55, 59
- wild aster, 54, 55
 - buckwheat, 53, 55
 - pennyroyal, 54, 55
 - red raspberry, 53
- willow, 53, 55
- yellow wood, 54, 55
- Honey-powders, 68
- Honeydew honey, 46, 51, 52, 55, 56, 60, 62, 65, 66
- Hormones, 520
 - insulin, 520
- Hydrocuminene, 423
- Hydrocyanic acid, 483
- Hydrogen number, 181
 - sulphide, 152
- Hydroquinone, 147
 - ethyl ester, 343
- Hydroxy-aldehyde, 492
- β -hydroxy- δ -methyl furfural, artificial
 - honey, 70
 - invert sugar sirup, 69
 - water mint, 234
- Hygrine, 86
- Hypoesterol, 487
- Hyssopus officinalis*, 220

I

Ilex, 87, 89, 91

- affinis*, 89
- amara longifoliaforma*, 89
- caroliniana*, 89
- Cassine myrtifolia*, 89
- chamædryfolia*, 89
- cognata*, 89
- congonhinha*, 89
- conocarpa*, 89
- cuyabensis*, 89
- diuretica*, 89

Ilex—(Cont.)

- dumosa Guaranina*, 89
- montevidensis*, 89
- glabra*, 89
- Glazioviana*, 89
- nigropunctata latifolia*, 89
- paltorioides*, 89
- paraguariensis*, 87, 89
- pseudothea*, 89
- symplociformis*, 89
- theezans fertilis*, 89
 - Riedellii*, 89
 - typica*, 89
- vitis idæa*, 89
- vomitorea*, 89
- Illicium anisatum*, 341
- religiosum*, 341
- verum*, 341
- Illipé butter, 131
- Indian mustard, 367, 372, 374
 - composition, 375
 - Jhuni, 375, 376
 - Kazli Sarishá, 375, 376
 - Lalki Tori, 375, 376
 - oil, fixed, 375
 - fatty acids, 376
 - oil, volatile, 376
 - phosphorus-organic compounds, 376
 - phytin, 376
 - structure, 375
- Indol, 402
- Ingwer, 198
- Inosine pyrophosphate, 497
- Inosinepyrophosphoric acid, 497
- Inositol, 92
- Insulin, 520
- Inulase, honey, 63
 - yeast, 513
- Inulin, 1
 - dandelion root, 174
 - chicory root, 172
- Inulo-coagulase, 172
- Invert sugar 1, 2, 3
 - honey, 48, 60
 - maple products, 42
 - sirup, *see* Invert sugar sirup
 - sugar beet products, 33
 - sugar cane products, 23
- Invert sugar sirup, 67
 - artificial honey, 68
 - composition, 68, 70
 - composition, 67
 - tests, 69
 - ash, 71
 - Browne's aniline acetate, 69

- Invert sugar sirup,
tests—(*Cont.*)
Föder's, 69
Fiehe's resorcinol-hydrochloric
acid, 69
Jägerschmid's acetone-hydrochloric
acid, 70
Ley's ammoniacal silver, 69
Lund's protein, 70
precipitin, 71
Invertase, cocoa, 126
honey, 63
yeast, 510
Iodine, coffee, 162
tea, 111
yeast, 524
4'-iododiphenylurethan, 104
Ionone, 197
Ipadu, 85
Ipecac, 139
Iridaceæ, 196
Iridin, 196
Iris family, flower spices, 278
rhizome spices, 196
Iris florentina, 196
Iron, cocoa, 135
coffee, 161
honey, 66
maté, 92
molasses, 24
sugar, 24
tea, 111
yeast, 523
Iron porphyratin, 502
Irone, 197
Isoapiole, 442
Isoborneol, 302
Isobutylaldehyde, 105
Isochavicic acid, 332
Isococamine, 86
Isoeugenol, 355
d-Isomenthone, 232
i-Isomenthone, 232
Isomyristicin, 426
Isopiperic acid, 332
Isopropyl-o-cresol, 242
Isopyrovitamin, xxv
Isosaccharosan, 77
Isotropylcocaine, 86
Isovaleraldehyde, 104, 105
Isovalerianate, 251
Isovaleric acid, 105, 229, 232
Japanese peppermint, 232
peppermint, 229
tea, 105
Isovaleryl alcohol, 190
aldehyde, citronella, 190
peppermint, 229
Isovanillin, 317
Isozingiberene, 210
- J
- Jambosa Caryophyllus*, 291
Japanese mint, *see* Japanese Pepper-
mint
Japanese peppermint, 219, 221, 225,
226, 229, 230, 231
oil, 231
constituents, 232
acetic acid, 232
acids, 232
camphene, 232
caproic acid, 232
caryophyllene, 232
dementholized, 233
ethylamylcarbinol, 232
formic acid, 232
furfural, 230
 α,β -hexenic acid, 232
 β,γ -hexenol, 232
d-isomenthone, 232
i-isomenthone, 232
l-limonene, 232
menthenone, 231, 232
isovaleric acid, 232
menthol, 232
l-menthol, 232
menthone, 232
l-menthone, 232
 α -pinene, 232
sesquiterpene, 232
d-sesquiterpene, 232
dl-sesquiterpene alcohol, 232
values, 231, 232
test for, 230
Jhuni, 375, 376
Juniper berry, 301, 320
composition, 301
oil, volatile, 301
constituents, 302
cadinene, 302
camphene, 302
isoborneol, 302
juniper camphor, 302
phellandrene, 302
 α -pinene, 302
d-sabinene, 302
terpineol, 302
values, 301

Juniper berry—(Cont.)
 pentosans, 302
 structure, 301
 Juniper camphor, 302
Juniperus communis, 301, 320

K

Kaffee, 140
 Kaffee Hag, 142, 153
 Kahweol, 153, 158
 Kai-choi, 377
 Kakao, 114
 Kalmuswurzel, 191
 Kämmer's porphyrin, 503
 Kapern, 283
 Kapuzinerkresse, 398
 Kardamomen, 303
 Karite butter, 131
 Kazli Sarishá, 375, 376
 Keto-aldehydes, 492
 β -Keto-1-gulofuranolactone, xxii
 Ketones, 442
 Ketoses, 5
 Kolanuss, 137
 Königspaprika, 443, 449
 Koriander, 416
 Krauseminze, 234
 Kreuzkümmel, 420
 Kubeben, 339
 Kümmel, 434

L

Labiatae, 219, 221
 Lactic acid, beet molasses, 33
 cane molasses, 22
 honey, 60
 yeast, 487, 489
 Lactoflavin, xxix
 Lactone, 229
 Lactose, 1, 8, 9
 Laevulin, 174
 Lalki Tori, 375, 376
 Lana batu, 189
 Langer Pfeffer, 336
Lauraceae, 215, 260, 357
 Laurel, 215
 Laurel family, bark spices, 260
 fruit spices, 357
 leaf spices, 215
 Lauric acid, nutmeg, 353
 orris, 197
 Lauro, 215
Laurus nobilis, 215, 217
Sassafras, 276

Leaf alkaloidals, 85
 Leaf spices, 187
 Leaven, 465
 Lecithin, cocoa, 135
 fenugreek, 393
 sugar cane products, 22
 yeast, 497, 498
 Legumes, 163, 389
Leguminosæ, 163, 389
 Lemon grass oil, 187
 constituents, 188
 citral, 188
 n-decylaldehyde, 188
 dipentene, 188
 farnesol, 188
 geraniol, 188
 limonene, 188
 linalool, 188
 methyl heptenol, 188
 methyl heptenone, 188
 myrcene, 188
 nerol, 188
 values, 187
 Lemon oil, 401, 403
 Australian, 404
 Calabrian, 404
 California, 403, 404
 constituents, 405
 acetic acid, 405
 bisabolene, 405
 l-camphene, 405
 capric acid, 405
 caprylic acid, 405
 citral, 405
 citronellal, 405
 citropene, 405
 dipentene, 405
 geranial, 405
 geranyl acetate, 405
 limonene, 405
 d-limonene, 401, 405
 l-limonene, 405
 linalyl acetate, 405
 methyl heptenone, 405
 nonylaldehyde, 405
 octyl aldehyde, 405
 i- α -pinene, 405
 l- α -pinene, 405
 l- β -pinene, 405
 β -phellandrene, 405
 sesquiterpenes, 405
 γ -terpinene, 405
 terpineol, 405
 Florida, 403
 values, 403

- Lemon oil—(*Cont.*)
 Sicilian, 403, 404
 standards, 404
 terpeneless, 406
- Lemongras, 187
- Leucine, beet molasses, 32
 sugar cane juice, 21
- Leucophyl, 161
- Levulose, 1-3, 9, 23
 nectar, 46
 sugar cane products, 23
- Lignin, 133
- Lima, 406
- Lime, 406
 oil, 406
 constituents, 407
d-limonene, 407
 linaloöl, 407
l-linalyl acetate, 407
 values, 406
- Limene, 402
- Limón, 403
- Limone, 403
- Limonene, caraway, 416
 celery, 416
 fennel, 416, 430
 grapefruit, 407
 lemon, 405
 grass, 188
 orange flower, 402
 spearmint, 236
- d*-Limonene, caraway, 438
 celery, 440
 dill, 426
 lemon, 401, 405
 lime, 407
 orange, 401
- l*-Limonene, citronella, 190
 Japanese peppermint, 232
 lemon, 405
 peppermint, 229
 Seychelles cinnamon, 275
 star anise, 343
- Limonia aurantifolia*, 406
- Linaloöl, basil, 221
 Ceylon cinnamon, 276
 clary, 221
 ginger, 209
 lemon grass, 188
 lime, 407
Ocimum gratissimum, 224
Origanum Smyrneum, 239
 sage, 251
 Saigon cassia, 271
 Seychelles cinnamon, 275
- Linaloöl—(*Cont.*)
 sweet basil, 223
 tea, 105
 thyme, 242
 water mint, 234
- d*-Linaloöl, cocoa, 132
 coriander, 419, 420
 nutmeg, 355
 orange, 401
- l*-Linaloöl, bay leaf, 218
 Ceylon cinnamon, 275, 276
 clary, 253, 254
Ocimum canum, 224
 orange flower, 402
 rose, 289
 spearmint, 236
 thyme, 242
- Linaloöl acetate, 221, 231, 234
- Linalyl acetate, bergamot, 402
 clary, 221, 253
 lemon, 405
 orange flower, 402
 sage, 251
- l*-Linalyl acetate, clary, 254
 lime, 407
- Linalyl isobutyrate, 275
- Linolenic acid, nutmeg, 353
 peppermint, 230
 water mint, 234
- Linolic acid, coffee, 157
 nutmeg, 353
 water mint, 234
- Lipase, 507
- Lipins, 393
- Lithium, 35
- Lomatia obliqua*, 90
- Long pepper, 319, 336; *see also* Black pepper
 composition, 330, 339
 mineral constituents, 336
 pentosans, 335, 336
 piperine, 319
 starch, 335
 structure, 337
- Lorbeerblatt, 215
- Löwenzahn, 173
- Lupeol, 234
- Lutein, 454
- Lycopene, capsicums, 460
 chillies, 460
- Lycopersin, capsicums, 460
 chillies, 460
- Lycopersicin, 454
- Lyperia crocea*, 276
- Lysine, 32

M

Macassar mace, 345-347, 351, 352
 nutmeg, 345, 349, 351, 352
 Mace, **345**
 Banda, 345-347, 352
 Batavia, 345, 352
 Bombay, 345-348, 351, 352
 composition, 348, 351, 352; *see also*
 Nutmeg
 oil, volatile, 354
 constituents, 354
 dipentene, 354
 myristic acid, 354
 myristicin, 354
 myristicol, 354
 phenols, 354
 pinene, 354
 values, 354
 East Indian, 351
 Macassar, 345-347, 351, 352
 microscopy, 348
 Papua, 345
 Penang, 345, 352
 structure, 345
 West Indian, 351
 Macerone, 173
 Macia, 345
 Macilenic acid, 354
 Maciloic acid, 354
 Macis, 345
 Madder family, seed alkaloidals,
 139
 Magnesium lactate, 33
 Magnolia family, fruit spices, 341
Magnoliaceæ, 341
 Maha pangiri, 189
 Maiorana, 236
 Maize glucose, 74
 malt sirup, 75
 Majoran, 236
Majorana hortensis, 236
 Malic acid, coffee, 159
 honey, 60
 maple sugar, 41
 nectar, 46
 sugar cane, 22
l-Malic acid, maple sand, 42
 maple sugar, 41
 Malt sirup, 75
 Malt sugar, 1
 Maltase, yeast, 512
 Maltodextrin, 74
 Maltose, 1, 3, 7, 9
 honey, 62

Mandarin orange oil, **403**
 constituents, 403
 values, 403
 Manganese, cocoa, 136
 fenugreek, 393
 honey, 66
 maple sugar, 44
 maté, 92
 molasses, 24
 tea, 111
 yeast, 523
 Mango-ginger, 211
 Mannan, coffee, 161
 yeast, 493
 Mannodextran, 494
 Mannose, coffee, 161
 yeast, 510
 α -*d*-Mannosidase, 161
 Maple products, **36**
 composition, 37-40
 constituents, 41
 acid, 41
 acetic, 41, 42
 citric, 41, 42
 formic, 41, 42
 fumaric, 41, 42
 malic, 41
 l-malic, 41, 42
 succinic, 41
 d-tartaric, 41, 42
 tricarballic, 41, 42
 vanillic, 42
 bacteria, 43
 carbohydrates, 42
 colors, 42
 coniferin, 42
 enzymes, 43
 amylase, 43
 flavor, 42
 guaiacol, 42
 hadromal, 42
 mineral, 43
 minor mineral, 44
 manganese, 44
 vanillin, 42
 various, 43
 manufacture, 36
 sap, 36
 sirup, 36
 standards, 37
 statistics, 36
 sugar, 36
 Maple sugar sand, 41, 42
 Marigold, 278
 Marjolaine, 236

- Marjoram, pot, 236, 237
 sweet, *see* Sweet Marjoram
 Marsh marigold, 283
 Masecuite, 12, 15, 31
 Mate, 87
 Maté, 87
 bombilla, 87
 composition, 90
 constituents, 91
 astringents, 92
 phlobaphene, 92
 inositol, 92
 purine bases, 91
 caffeine, 91
 matésterol, 92
 mineral, 92
 minor mineral, 92
 iron, 92
 manganese, 93
 tannin, 92
 key, 89
 preparation, 87
 species, 87
 structure, 88
 Matésterol, 92
 Mediterranean mint, 231
 linaloöl, 231
 menthol, 231
 Meiorana, 236
 Melezitose, 62
Melilotus, 394
 Melisse indienne, 187
 Melissic acid, peppermint, 230
 water mint, 234
 Melitriose, *see* Raffinose
 Menta, 234
 piperita, 224
 verte, 234
Mentha, 231
 aquatica, 233, 235
 arvensis, 225 55,
 piperascens, 231
 canadensis, oil, 231
 citrata, oil, 231
 crispa, 225
 longifolia, 236
 mirennæ, oil, 231
 piperita, 224, 230
 austriaca, 229
 Pulegium, oil, 231
 hirsuta, oil, 231
 silvestris, 225
 spicata, 225, 234
 viridis, 234
 Menthe crépue, 233
 poivrée, 224
 verte, 234
 Menthene, 229
 Mentheneone, Japanese peppermint,
 231, 232
 peppermint, 229
 Menthol, 185, 229
 Japanese peppermint, 221, 232
 peppermint, 221, 231
l-Menthol, Japanese peppermint, 232
 peppermint, 228, 229
 Menthone, 230
 Japanese peppermint, 221, 232
 peppermint, 221, 230
d-Menthone, 229
l-Menthone, Japanese peppermint, 232
 peppermint, 228, 229
 Menthyl acetate, 182
 esters, 229
 Mesotartaric acid, 526
 Methanol, 490
o-Methoxybenzoic acid, 103
 Methoxybenzylmethylketone, 434
o-Methoxycinnamaldehyde, 265
3-Methoxy-4-hydroxy-phenyl-ethyl-
 methyl ketone, 207
 Methyl acetylcarbinol, 153
 Methyl alcohol, cloves, 298
 tea, 105
 Methyl amine, 147
 water mint, 234
 Methyl-*n*-amyl carbinol, 298
 Methyl-*n*-amylketone, Ceylon cinna-
 mon, 275
 cloves, 298
 Methyl anthranilate, grapefruit, 407
 honey, 65
 orange, 401
 orange flower, 402
 Methyl benzoate, 298
 β -Methyl-butan- α -ol, 104
 Methyl chavicol, anise, 416, 433, 434
 basil, 221
 fennel, 430
 Ocimum gratissimum, 224
 star anise, 343
 sweet basil, 223
 tarragon, 257
 Methyl cinnamate, 224
 Methyl eugenol, 184
 allspice, 412
 bay leaf, 218
 calamus, 194
 citronella, 190

- α -Methyl furfural, 298
- Methyl glyoxalase, 518
- Methyl heptenol, 188
- Methyl heptenone, citronella, 190
 - ginger, 209
 - lemon, 405
 - grass, 188
- Methyl-*n*-heptyl carbinol, 298
- Methyl heptylketone, 298
- Methylisopropylphenol, 242
- 7-Methyl-mannityl-alloxazine, xxix
- Methyl mercaptan, 152
- 8-Methyl-2-nonen-1-aldehyde, 420
- Methyl ortho-coumaraldehyde, 266, 267
- n*-Methylpyrrole, 152
- Methyl salicylaldehyde, 266
- Methyl salicylate, 182, 184, 259
 - birch, 259
 - tea, 104, 105
 - wintergreen, 259
- Methyleneprotocatechuic acid, 317
- Methyleneprotocatechuic aldehyde, 318
- Methylprotocatechuic aldehyde, 316
- Methylpyrroline, 335
- Mineral constituents, *see* individual products
- Minor mineral constituents, chicory
 - root, 173
 - cocoa, 135, 136
 - coffee, 161, 162
 - fenugreek, 393
 - honey, 66
 - maple sugar, 44
 - maté, 92
 - molasses, 24, 35
 - saffron, 282
 - sugar cane products, 18, 24
 - tea, 111
 - yeast, 523, 524
- Mint, bergamot, *see* Bergamot mint
- family, leaf spices, 219
- Japanese, *see* Japanese peppermint
- Mediterranean, *see* Mediterranean mint
- water, *see* Water mint
- wild, 231
- Mogdadkaffee, 163
- Molasses, beet, *see* Sugar beet products
- cane, *see* Sugar cane products
- Monardeæ*, 219
- Monocarboxylic acid, 355
- Mostarda bianca, 378
 - hera, 363
- Mostarde bruna, 372
- Mostaza baza, 372
 - blanca, 378
 - negra, 363
- Moutarde blanche, 378
 - brune, 372
 - noire, 363
 - sauvage, 384
- Mucilage, 393
- Muscatel sage, *see* Clary
- Muskateller Salbei, 252
- Muskatnuss, 349
- Mustard, 361
 - black, *see* Black mustard
 - brown, *see* Brown mustard
 - cake, 362
 - Chinese, *see* Chinese mustard
 - Danish, 372
 - flour, 361, 362
 - Indian, *see* Indian mustard
 - prepared, 362, 363
 - Sarepta, 363, 372, 375; *see also* Brown mustard
 - seed, 362
 - standards, 362
 - white, *see* White Mustard
 - wild, 372, 374, 384, 385, 388
- Mustard family, seed spices, 361
- Myrcene, 188
- Myrcia*, 408
- Myrcia oil, 413
- Myrica oil, 217
- Myristic acid, coffee, 157
 - mace, 354
 - nutmeg, 355
 - orris, 197
 - water mint, 234
- Myristica*, 353
 - argentea*, 345, 349
 - fragrans*, 345, 349, 351
 - malabarica*, 345, 349
- Myristicaceæ*, 345
- Myristicin, dill, 426
 - mace, 354
 - nutmeg, 353
 - parsley, 442
- Myristicol, 354
- Myristin, 353
- Myrosin, black mustard, 370, 271
 - white mustard, 382
- Myrosinase, 370
- Myrtaceæ*, 291, 408
- Myrtle family, flower bud spices, 291
- fruit spices, 408
- Myrtus*, 408
 - Pimenta*, 408

N

- Naphthalene, 197
 α -Naphthylurethan, 104
 Naranja, 399
 Nasturcio, 398
 Nasturtium, 283, **398**
 structure, 398
 Nasturtium family, fruit spices, 398
 Nasturzio, 398
 Nectar, floral, 45, 56
 Neosterol, 486
 Nerol, bergamot, 402
 citronella, 190
 lemon grass, 188
 orange flower, 402
 rose, 289
 Neroli camphor, 402
 oil, 401; *see also* Orange flower oil
 Nerolidol, 402
l-Nerolidol, 254
 acetate, 254
 Nicotinic acid, xxi, xxix
 yeast, 490
 Nightshade family, fruit spices, 443
Nipa fruticans, 28
 Nipa palm sugar, 28
 Niter, 36
 Nitrates, 32
 Noce moscada, 349
 Noix de bétel, 112
 de kola, 137
 muscade, 349
 Nonaldehyde, Ceylon cinnamon, 275
 ginger, 209
 lemon, 405
 rose, 289
 Seychelles cinnamon, 276
n-Nonoic acid, 132
 Nonylic acid, 197
 alcohol, 401
 Nucleates, 499
 Nucleic acid, history, 498
 nucleates, 499
 nucleins, 499
 properties, 499
 yeast, 490, 498
 Nucleins, 499
 Nucleoalbumin, 393
 Nucleoprotein, 392
 Nuez moscada, 349
 Nutmeg, 345, **349**
 Banda, 349
 butter, 351

Nutmeg—(Cont.)

- carbohydrates, 356
 amylodextrin starch, 356
 pentosans, 356
 Ceylon, 355
 colors, 356
 xanthophyl, 356
 composition, 351, 352
 East Indian, 351
 limed, 351
 long, 349, 351
 Macassar, 345, 349, 351, 352
 oil, fixed, 351
 constituents, 353
 acetic acid, 353
 cerotic acid, 353
 formic acid, 353
 lauric acid, 353
 linolenic acid, 353
 linolic acid, 353
 macilenic acid, 353
 maciloic acid, 354
 myristic acid, 353
 myristicin, 353
 myristin, 353
 oleic acid, 353
 olein, 353
 palmitic acid, 353
 phytosterol, 353, 354
 resins, 353
 trimyristin, 353
 triolein, 353
 tripalmitin, 353
 values, 352
 oil, volatile, 354
 constituents, 354
 alcohols, 355
 aldehyde, 355
 d-borneol, 355
 camphene, 355
 d-camphene, 355, 356
 p-cymene, 355
 dipentene, 355, 356
 esters, 355
 eugenol, 355
 geraniol, 355
 isoeugenol, 355
 d-linaloöl, 355
 monocarboxylic acid, 355
 myristic acid, 355
 myristicin, 355
 pinene, 355
 α -pinene, 355
 β -pinene, 355
 d-pinene, 355, 356

Nutmeg,
 oil, volatile,
 constituents—(Cont.)
 safrole, 355
 terpenes, 355
 terpineol, 355
 α -terpineol, 355
 d-terpineol, 355
 i-terpineol, 355
 values, 354
 Padang, 349, 351, 352
 Papua, 345
 Penang, 349, 351, 352
 Singapore, 349, 351, 352
 standards, 351
 structure, 349
 West Indian, 349, 351
 Nutmeg cardamom, 303
 family, seed spices, 345

O

Ocimene, *Ocimum gratissimum*, 224
 sweet basil, 223
 tarragon, 257
Ocimoideæ, 219
Ocimum, 223
 americanum, 224; see also *O. canum*
 basilicum, 221
 canum, 224
 oil, volatile, 224
 alcohols, 224
 allocinnamate, 224
 d-camphor, 224
 esters, 224
 estragol, 224
 eucalyptol, 224
 geraniol, 224
 l-linaloöl, 224
 methyl cinnamate, 224
 d-sesquiterpene, 224
 l-sesquiterpene, 224
 values, 224
 gratissimum, 224
 oil, volatile, 224
 alcohols, 224
 esters, 224
 eugenol, 224
 linaloöl, 224
 methyl chavicol, 224
 ocimene, 224
 phenols, 224
 phenyl ethers, 224
 terpenes, 224
Ocimum—(Cont.)
 minimum, 221
 sanctum, 224
 oil, volatile, 224
 chavibetol, 224
 eugenol, 224
 phenols, 224
 values, 224
 viride, 223, 224
 oil, volatile, 223
 phenols, 223
 α -terpinene, 223
 γ -terpinene, 223
 thymol, 223
 values, 224
 Octanol, 105
 Octoic acid, 132
 Octyl alcohol, grapefruit, 407
 orange, 401
n-Octyl alcohol, 104
 Octyl aldehyde, grapefruit, 407
 lemon, 405
 Octylic acid, 197
 Oenanthaldehyde, 259
 Oil, see individual products
 fixed, see individual products
 volatile, see individual products
 Oleic acid, coffee, 157
 nutmeg, 353
 orris, 197
 peppermint, 230
 water mint, 234
Oleum cinæ, 213
 Orange douce, 399
 Orange flower oil, 401
 constituents, 402
 acetic acid, 402
 aurode, 402
 benzoic acid, 402
 l-camphene, 402
 decyl aldehyde, 402
 dipentene, 402
 farnesol, 402
 geraniol, 402
 indol, 402
 limonene, 402
 l-linaloöl, 402
 linalyl acetate, 402
 methyl anthranilate, 402
 nerol, 402
 neroli camphor, 402
 nerolidol, 402
 palmitic acid, 402
 phenyl acetic acid, 402
 phenyl ethyl alcohol, 402

Orange flower oil,
 constituents—(*Cont.*)
 l- α -pinene, 402
 α -terpineol, 402
 values, 401
 Orange oil, bitter, 401
 flower, 401; *see also* Orange flower
 oil
 mandarin, 403
 sweet, 399; *see also* Sweet orange
 tangerine, 403
Origanum hirtum, oil, 239
 Majorana, 236
 majoranoides, oil, 239
 Maru, oil, 240
 Smyrneum, oil, 239
 virens, oil, 239
 vulgare, 236
 Orris, 196
 composition, 196
 iridin, 196
 oil, volatile, 196
 constituents, 197
 benzaldehyde, 197
 benzoic acid, 197
 capric acid, 197
 caprylic acid, 197
 decyllic acid, 197
 n-decylaldehyde, 197
 duodecyllic acid, 197
 furfural, 197
 ionone, 197
 irone, 197
 lauric acid, 197
 myristic acid, 197
 naphthalene, 197
 nonylic acid, 197
 nonylic aldehyde, 197
 octylic acid, 197
 oleic acid, 197
 pelargonic acid, 197
 tridecyllic acid, 197
 undecyllic acid, 197
 values, 196
 structure, 196
 Orchid family, spices, 308
Orchidaceæ, 308
 Oryzanin, xxi
 Otto of roses, 287, 288
 Ovalbumin, xxxii
 Oxalic acid, black pepper, 335
 cane juice, 22
 chicory root, 172
 cocoa, 132
 coffee, 159

Oxalic acid—(*Cont.*)
 nectar, 46
 sugar cane, 22
 tea, 105
 Oxidase, ascorbic acid, xxiii
 cocoa, 126
 honey, 63, 64
 tea, 109
 Oxidizing enzymes, 519
 yellow, 519
 yellow-red, 519
 Oxyhydroxycymene, 242
 Oxytheotannin, 109

P

Palai, 366; *see also* Indian mustard
 Palm family, seed alkaloidals, 112
 stalk products, 28
 date palm sugar, 28
 nipa palm sugar, 28
 palmyra palm sugar, 28
 sugar palm sugar, 2, 28
Palmaceæ, 112
 Palmitic acid, allspice, 412
 calamus, 194
 celery, 440
 coffee, 147, 157
 nutmeg, 353
 orange flower, 402
 parsley, 442
 peppermint, 230
 tea, 103, 105
 water mint, 234
 Palmitostearoölein, 130
 Palmyra palm sugar, 28
 Paprika, xxx, 443
 acids, 452
 ascorbic, 452
 African, 452
 capsaicin, 452
 carbohydrates, 453
 pentosans, 453
 sucrose, 453
 colors, 453
 capsanthin, 453, 454
 capsorubin, 454
 carotene, 454
 citraurin, 454
 citrin, xxx
 cryptoxanthin, 454
 lycopersicin, 454
 lutein, 454
 values, 454

- Paprika,
 colors—(*Cont.*)
 xanthophyl, 454
 zeaxanthin, 454
 composition, 447, 448
 changes during growth, 449
 Georgian, 451
 Hungarian, 443, 447, 449, 451, 452, 460
 Japan, 453
 Königspaprika, 443, 449
 Manchurian, 453
 microscopy, 447
 mineral constituents, 454
 oil, fixed, 450
 values, 451
 oil, volatile, 451
 Rose, 454
 Rosenpaprika, 443, 449
 Silesian, 449
 Spanish, 443, 447, 449, 451, 460
 standards, 449
 structure, 444
 sweet, 443, 451, 455
 vitamin P, xxx
 Paradol, 207
 Parahydroxybenzyl isothiocyanate, 382
 Para-methoxypropylbenzene, 434
 Paraoxy-metamethoxy-allyl benzene, 298
 Parsley camphor, 442
 family, 414
 fruit spices, 414
 Parsley seed, 416, 441
 composition, 441
 oil, fixed, 441
 oil, volatile, 441
 constituents, 442
 aldehydes, 442
 apiole, 416, 442
 ketones, 442
 myristicin, 442
 palmitic acid, 442
 parsley camphor, 442
 petrosilane, 442
 phenols, 442
 values, 441
 structure, 441
Paullinia Cupana, 113
 sorbilis, 113
 Pea family, coffee substitutes, 163
 seed spices, 389
 Pectic acid, cocoa, 133
 sugar beet products, 33
 Pelargonic acid, 197
 Pennyroyal, 231
 Pentosans, *see* individual products
 Pepe, 319
 di Caienna, 455
 Peperone, 336, 443
 Pepper, 319
 black, *see* Black pepper
 cayenne, *see* Cayenne pepper
 family, 319
 fruit spices, 319
 long, *see* Long pepper
 red, 447
 tree, 320
 white, 320; *see also* Black pepper
 Peppermint, 219, 221, 224, 231, 234
 American, 227, 231
 ash, 230
 Australian, 226
 betaine, 230
 British East Africa, 226
 Caucasus, 226
 composition, 226
 dextrose, 230
 English, 225, 227, 230
 Esthonian, 226
 French, 226, 230
 German, 226
 glycerol, 230
 hesperetin, 230
 hesperidin, 230
 Hungarian, 226
 Irish, 226
 Italian, 226
 Japanese, *see* Japanese peppermint
 Kenya, 227
 key, 221
 linolenic acid, 230
 melissic acid, 230
 Mitcham, 225, 229, 230
 oil, 226
 constituents, 228
 acetic acid, 229
 aldehyde, 229
 amyl alcohol, 229
 cadinene, 229
 cineol, 229
 dimethyl sulphide, 229
 isovaleraldehyde, 229
 isovaleric acid, 229
 lactone, 229
 l-limonene, 229
 menthene, 229
 menthenone, 229
 menthol, 231
 l-menthol, 228, 229

- Peppermint,
oil,
 constituents—(*Cont.*)
 menthone, 230
 d-menthone, 229
 l-menthone, 228, 229
 menthyl esters, 229
 phellandrene, 229
 i-pinene, 229
 d-piperitone, 229
 pulegone, 229
 terpinene, 229
 standards, 228
 terpeneless, 230
 values, 226, 227
oleic acid, 230
Palestine, 226
palmitic acid, 230
pentosans, 230
phytosterol, 230
phytosterolin, 230
rhamnose, 230
Russian, 226, 229
stearic acid, 230
structure, 225
Pepsin, 505
Peptidase, 505
Perejil, 441
Peroxidase, honey, 63, 64
 tea, 109
Persil, 441
Petersilie, 441
Petrosilane, 442
Petroselinum sativum, 441
Pfeffer, 319
Pfefferminze, 224
Phellandrene, 182
 Brisbane sassafras, 268
 coriander, 419
 turmeric, 213
Phellandrene, anise, 434
 black pepper, 335
 Ceylon cinnamon, 276
 dill, 426
 juniper berry, 302
 peppermint, 229
 sassafras, 277
 tarragon, 257
 α -Phellandrene, anise, 434
 fennel, 430
 ginger, 210
 β -Phellandrene, ginger, 209, 210
 lemon, 405
 Seychelles cinnamon, 275
 star anise, 343
d- α -Phellandrene, 213
l-Phellandrene, Ceylon cinnamon, 275
 spearmint, 236
l- α -Phellandrene, allspice, 412
 star anise, 343
Phenols, Brisbane sassafras, 268
 celery, 440
 coffee, 158
 mace, 354
 Ocimum gratissimum, 224
 sanctum, 224
 viride, 223
 parsley, 442
 spices, 182, 184
 tea, 104
 Thymus capitatus, 243
 odoratissimus, 243
Phenyl alcohol, orange flower, 402
 tea, 104, 105
 ethers, *Ocimum gratissimum*, 224
Phenylacetic acid, orange flower, 402
 tea, 105
Phenylethanol, 105
 β -Phenyl-ethyl alcohol, 289
Phenyl-propyl acetate, 266
Phenyl-propyl aldehyde, 275
Phenylurethan, 218
Phlobaphene, 92
Phœnix dactylifera, 28
Phosphatase, black mustard, 371
 white mustard, 371
 yeast, 518
Phosphate baking powder, 527
Phosphodihydroacetone, 495
Phosphoglyceraldehyde, 495
2-Phosphoglyceric acid, 495
3-Phosphoglyceric acid, 495
 α -Phosphoglycerol, 495
Phosphopyruvic acid, 495
Phosphoric acid, 60, 66
Phosphorus-organic compounds, *see*
 individual products
Phytase, 520
Phytin, black mustard, 371
 charlock, 388
 fenugreek, 393
 Indian mustard, 376
 white mustard, 383
Phytosterol, nutmeg, 353, 354
 peppermint, 230
 water mint, 234
Phytosterolin, 230
Picante, 455
Picrocrocine, 281

- Piment, 408
 de la Jamaïque, 408
 des jardins, 443
Pimenta acris, 217, 408, 413
 officinalis, 408
 Pimento, 408
 leaf oil, 412
 Pimenton, 449
 Pimienta de Castilla, 319
 larga, 336
 Pimiento, 443, 447, 449, 453
 composition, 448, 451
Pimpinella Anisum, 430
Pinaceæ, 301
 Pine family, fruit spices, 301
 Pinene, 182, 185
 Brisbane sassafras, 268
 calamus, 195
 Ceylon cinnamon, 276
 cubebs, 340
 formula, structural, 185
 mace, 354
 nutmeg, 355
 rosemary, 221
 sage, 251
 sassafras, 277
 Summer savory, 246
 α -Pinene, bay leaf, 218
 bergamot, 402
 Japanese peppermint, 232
 juniper berry, 302
 nutmeg, 355
 rosemary, 248
 spearinint, 236
 Thymus marschallianus, 243
 β -Pinene, bay leaf, 218
 coriander, 419
 nutmeg, 355
 Seychelles cinnamon, 275
 thyme, 242
 d -Pinene, fennel, 430
 nutmeg, 355, 356
 d - α -Pinene, anise, 434
 calamus, 194
 coriander, 419
 sage, 251
 star anise, 343
 sweet basil, 223
 dl - α -Pinene, 419
 i -Pinene, 229
 i - α -Pinene, 405
 l -Pinene, 242
 l -Pinene, Ceylon cinnamon, 275
 lemon, 405
 orange flower, 402
 l - β -Pinene, 405
Piper Bètte, 112
 Cubeba, 339
 longum, 336, 337
 nigrum, 319
 officinarum, 336
Piperaceæ, 319, 389
 Piperic acid, 332
 Piperidine, 335
 Piperine, black pepper, 319, 331, 332
 long pepper, 319
 Piperitone, 231
 d -Piperitone, 229
 Piperonal, 318
 Poivre, 319
 cubèbe, 339
 de Cayenne, 455
 long, 336
 Pollen, 48, 50
 histology, 49
 honey, 48
 Polychroit, 282
 Polypeptidase, 506
 Polysaccharides, yeast, 495
 Pomo di paradiso, 407
 Pompelmouse, 407
 Pompelmus, 407
 Porphyrin, 503
 Pot marjoram, 236, 237
 Potassium bitartrate in baking powder,
 525
 caffeine chlorogenate, 160
 myronate, black mustard, 370
 brown mustard, 370
 nitrate, 234
 Potato glucose, 73, 74
 malt sirup, 75
 Prezzemolo, 441
 Propionic acid, tea, 103, 105
 yeast, 487
 Protease, cocoa, 126
 honey, 63, 64
 yeast, 505
 Proteinase, 505, 506
 Proteins, *see* individual products
 Protocatechuic acid, 343
 Provitamin A, *see* Carotene
 Pulegone, pennyroyal, 231
 peppermint, 229
 Satureia nepeta, 246
 Purine, alkaloidal products, 82
 Purine bases, alkaloidal products, 81
 cocoa, 128
 coffee, 154
 cola nut, 138

Purine bases—(Cont.)

- maté, 91
- sugar cane products, 22
- tea, 102
- yeast, 483
- Pyran, 7
- Pyrazine, 152
- Pyridine, 152, 155
- Pyrimidine bases, alkaloidal products, 84
 - yeast, 483
- Pyrocalciferol, xxv
- Pyrophosphatase, 519
- Pyrophosphate baking powder, 528
- Pyracemic acid, 487
- Pyrrolic acid, 487
- Pyrrol, 147, 155
- Pyrus malus*, 55
- Pyruvic acid, yeast, 487

Q

- Quercetin, 109
- Quercus alba*, 55
- Quinic acid, 159, 160
- Quinoidine, 501
- Quinoline, 105

R

- Racemic acid, 526
- Racine de chicorée, 167
- Radice di iris, 196
- Raffinase, 126
- Raffinose, 1, 3, 8, 9
 - sugar beet products, 33
- Rái, 374
- Raiz de iris florentina, 196
- Rapanea guyanensis*, 90
 - laevirens*, 90
 - matensis*, 90
- Rape, 364
 - cake, 369, 370
 - common, 363, 367
 - German, 363, 367
 - oil, 368, 369, 380
 - proteins, 380
 - globulin, 380
- Red pepper, Hungarian, 447
 - Silesian, 449
 - Spanish, 447
- Reductase; *see also* Dehydrogenase
 - honey, 63, 64
 - yeast, 507, 508, 518

- Resins, nutmeg, 353
 - Thymus marschallianus*, 213
 - vanilla, 318
- Resorcin, 148
- Resorcin-hydrochloric acid test, 69
- Reuniol, 289
- Rhamnose, peppermint, 230
 - water mint, 234
- Rhizoma calami*, 191
- Rhizome d'iris, 196
- Rhizome spices, calamus, 191
 - ginger family, 198
 - orris, 196
- Rhodinol, 288, 289
- Riboflavin, xxi, xxvii, xxix
 - yeast, 504, 505, 520
- Robison ester, 474, 495, 496, 517
- Romarin, 246
- Romero, 246
- Roots, composite family, 167
- Rosa, 287
- Rosa*, 287
 - alba*, 287
 - canina*, 288
 - centifolia*, 287
 - damascena*, 287, 288
 - alba*, 288
 - gallica*, 288
 - trigintipetala*, 287
- Rosaceæ, 287
- Rose, 287
 - Bulgarian, 287-289
 - composition, 287
 - extract, 288
 - German, 287
 - Italian, 288
 - oil, 287
 - constituents, 288
 - citral, 289
 - citronellol, 288, 289
 - esters, 289
 - farnesol, 289
 - geraniol, 288, 289
 - l*-linalool, 289
 - nerol, 289
 - nonylaldehyde, 289
 - β -phenyl-ethyl alcohol, 289
 - reuniol, 289
 - rhodinol, 288, 289
 - roseol, 289
 - stearoptene, 288
 - terpenes, 289
 - standards, 288
 - values, 287
- Russian, 289

Rose family, flower spice, 287
 paprika, 454
 Rosemary, 219, 221, 246
 composition, 247
 key, 221
 oil, volatile, 247
 constituents, 248
 borneol, 221, 248
 bornyl acetate, 248
 camphene, 248
 camphor, 248
 camphylene, 248
 caryophyllene, 248
 cineol, 248
 α -pinene, 248
 values, 247, 248
 structure, 247
 Rosenpaprika, 443, 449
 Roseol, 289
 Rosmarin, 246
 Rosmarino, 246
Rosmarinus officinalis, 246
 Rozspaprika, 449
Rubiaceæ, 139
Rudgea major, 90
 myrsinifolia, 90
 Rue family, fruit spices, 399
Ruta graveolens, 284
Rutaceæ, 399

S

Sabinene, cardamom, 307
 Thymus marschallianus, 243
d-Sabinene, 302
 Saccharine products, 1
 chemical constitution, 4
 gossypose, 8
 hexoses, 5
 lactose, 8
 maltose, 7
 melitriose, 8
 raffinose, 8
 sucrose, 5
 chemical reactions, 9
 physical properties, 2
 crystallization, 2
 polarization, 3
 multirotation, 4
 solubility, 3
 sweetness, 3
 statistics, 2
Saccharomyces, 520
 anamemsis, 502

Saccharomyces—(Cont.)
 cerevisiæ, 477
 theobromæ, 126
 Saccharophosphatase, 518, 519
Saccharum officinarum, 10
 Safflower, 278
 mineral constituents, 282
 Saffron, 278
 adulterants, 278
 carbohydrates, 281
 pentosans, 281
 colors, 281
 crocin, 282
 crocine, 281
 polychroit, 281
 composition, 279
 enzymes, 282
 emulsin, 282
 glucoside, 281
 mineral constituents, 282
 minor mineral constituents, 282
 boron, 282
 oil, volatile, 280
 constituents, 281
 picrocrocine, 281
 sativol, 281
 stearoptene, 281
 values, 280
 pentosans, 281
 standards, 280
 structure, 279
 Safran, 278
 Safrene, 277
 Safrole, 182, 184, 277
 Brisbane sassafras, 268
 Ceylon cinnamon, 276
 Cinnamomum Massoia, 269
 parthenoxylon, 269
 nutmeg, 355
 sassafras, 277
 shikimi, 343
 star anise, 343
 Sage, 219, 221, 249
 clary, 252
 composition, 250
 key, 221
 muscatel, *see* Clary
 oil, volatile, 250
 constituents, 251
 borneol, 221, 251
 camphene, 251
 d-camphor, 251
 cineol, 251
 dipentene, 251
 isovalerianate, 251

- Sage,
 oil, volatile,
 constituents—(Cont.)
 linalool, 251
 linalyl acetate, 251
 pinene, 251
 d- α -pinene, 251
 salvene, 251
 salviol, 251
 thujone, 221, 251
 values, 250
 pentosans, 252
 standards, 250
 structure, 249
 Saigon cassia, 260, 261, 263, 264, 270
 composition, 264, 271
 oil, volatile, 271
 aldehydes, 271
 eucalyptol, 271
 eugenol, 271
 linalool, 271
 structure, 270
 Saigon-Zimt, 270
 Salbei, 249
 Salicylaldehyde, 266
 Salicylic acid, 182
 China cassia, 266
 cloves, 298
 tea, 104, 105
 Saligenin, 491
 Sassafras, 276
 Salvene, 251
 Salyia, 249
Salvia bracteata, 252
 officinalis, 55, 249
 Sclarea, 252
 Salviol, 251
 Sanka, 142, 153
 Santoreggia, 244
Sapindaceæ, 113
 Saponin, shikimi, 344
 star anise, 344
 tea, 108
 Sarepta mustard, 372
 Sarepta-Senf, 372
Sarothamnus scoparium, 283
 Sariette, 244
 Sarson, 363, 367
 brown, 367
 Sassafras, 258, 260, 276
 bark, 258, 260
 Brisbane, 268
 colors, 276
 sassafrid, 276
 Sassafras,
 colors—(Cont.)
 sassafrin, 276
 sassarubin, 276
 composition, 276
 oil, volatile, 276
 constituents, 277
 d-camphor, 277
 eugenol, 277
 phellandrene, 277
 pinene, 277
 safrene, 277
 safrole, 277
 sesquiterpenes, 277
 values, 277
 root, 277
Sassafras officinale, 276
 variifolium, 276
 Sassafrid, 276
 Sassafrin, 276
 Sassarubin, 276
 Sativol, 281
Satureia Calamintha, oil, 246
 hortensis, 244
 montana, oil, 244, 246
 nepeta, oil, 246
 Thymba, oil, 246
Satureineæ, 219
 Sauge sclarée, 252
 Savory, Summer, *see* Summer savory
 Winter, *see* Winter savory
 Scandium, 35
Schinus molle, 320
 Schwarzer Senf, 363
 Sclareol, 221, 253
 Scotch broom, 283
Scutellaria albida, 220
 Sedanolide, celery, 416, 440, 441
 Sedanonic acid anhydride, celery, 440,
 441
 Seed alkaloidals, betel nut, 112
 cocoa, 114
 coffee, 140
 cola, 137
 guarana, 113
 Seed spices, 301
 mustard family, 361
 nasturtium, 398
 nutmeg family, 345
 pea family, 389
 Selinene, 441
 Sellerie, 438
 Seminase, 393
 Senape selvatica, 384
Serenoa serrulata, 55

- Serepta-Senf, 372
 Sesquiterpene, bay leaf, 218
 calamus, 194
 celery, 440
 citronella, 190
 clary, 254
 grapefruit, 407
 Japanese peppermint, 232
 lemon, 405
 sassafras, 277
 spices, 182
 Thymus marschallianus, 243
 water mint, 234
 wild cassia, 268
 d-Sesquiterpene, Japanese peppermint, 232
 Ocimum canum, 224
 l-Sesquiterpene, *Ocimum canum*, 224
 dl-Sesquiterpene alcohol, 232
 Seychelles cinnamon, 264, 273
 bark, 275
 composition, 264, 273
 leaf, 275
 oil, volatile, 273, 274
 constituents, 274
 aldehydes, 274
 benzaldehyde, 275
 camphene, 275
 camphor, 275
 caryophyllene, 275
 cinnamal, 274, 275
 cymene, 275
 eugenol, 274, 275
 l-limonene, 275
 linalool, 275
 nonylaldehyde, 275
 β -phellandrene, 275
 β -pinene, 275
 values, 274, 275
 Shagaol, 208
 Shikimene, 343
 Shikimi, 277, 341-344
 acids, 343
 protocatechuic, 343
 shikimic, 343, 344
 composition, 342
 oil, fixed, 342
 oil, volatile, 343
 anethole, 343
 safrole, 343
 saponin, 344
 shikimene, 343
 shikimin, 343, 344
 shikimipicrin, 343
 shikimol, 277, 343
 Shikimic acid, shikimi, 343, 344
 star anise, 344
 Shikimin, shikimi, 343, 344
 star anise, 344
 Shikimipicrin, 343
 Shikimol, 343
 Sinalbin, spices, 183
 white mustard, 382
 Sinalbin mustard oil, 382
 Sinapin, 383
 Sinapinic acid, 383
Sinapis alba, 362, 378
 arvensis, 384
 chinensis, 377
 juncea, 372, 375
 nigra, 363
 ramosa, 375
 Sinigrin, black mustard, 370
 brown mustard, 370
 white mustard, 381
 Sirup, cane, *see* Sugar cane products
 glucose, *see* Glucose sirup
 invert, *see* Invert sugar sirup
 malt, 75
 maple, *see* Maple products
 sorghum, *see* Sorghum products
 Soapberry family, seed alkaloids, 113
 Soda alum in baking powder, 525
 Sodium acid pyrophosphate in baking powder, 526
 aluminum sulphate in baking powder, 526
 bicarbonate in baking powder, 465, 525
 Solanaceæ, 443
Sophora japonica, 284
 Sorghum products, 25
 color, 26
 composition, 25, 26
 juice, 25
 mineral constituents, 26
 sirup, 25
 stalks, 2
 standards, 26
Spartium scoparium, 283
 Spearmint, 219, 221, 225, 231, 234
 American, 235
 composition, 235
 European, 235
 key, 221
 oil, 235
 constituents, 236
 acetic acid, 236
 carvone, 231, 236
 l-carvone, 236

- Spearmint,
 oil,
 constituents—(*Cont.*)
 cineol, 236
 dihydrocarveol, 231, 236
 dihydrocuminic alcohol, 236
 dipentene, 236
 limonene, 236
 l-linalool, 236
 l-phellandrene, 236
 α -pinene, 236
 standards, 235
 values, 235
 structure, 234
 Spices, **177**
 constituents, 178
 ash, 183
 cell wall material, 183
 ether extract, 183
 flavoring principles, 183
 nitrogenous constituents, 183
 oil, fixed, 178
 oil, volatile, 179
 acids, 182
 alcohols, 182
 aldehydes, 182
 esters, 180, 182
 hydrogen number, 181
 phenols, 182, 184
 sesquiterpenes, 182
 sulphides, 182
 terpenes, 181, 185
 thiocyanates, 182
 values, 179
 soluble carbohydrates, 183
 starch, 183
 Spurge, caper, 283
 Squalene, 486
 Standards, *see* individual products
 Star anise, **341**, 433
 acids, 343
 shikimic, 344
 composition, 342
 Japanese, 344
 oil, fixed, 342
 oil, volatile, 343
 constituents, 343, 433
 anethole, 343
 anisaketone, 343, 433
 cineol, 343
 p-cymene, 343
 p-cymol, 343
 dipentene, 343
 hydroquinone ethyl ester, 343
 l-limonene, 343
 Star anise,
 oil, volatile,
 constituents—(*Cont.*)
 methyl chavicol, 343
 β -phellandrene, 343
 l- α -phellandrene, 343
 d- α -pinene, 343
 safrole, 343
 α -terpineol, 343
 values, 343
 pentosans, 344
 saponin, 344
 toxic substances, 343
 shikimin, 344
 standards, 342
 structure, 341
 Starch, 1, *see also* individual products
 nectar, 46
 Starch sugar, **72**
 composition, 73
 maize, 74
 manufacture, 72
 potato, 74
 standards, 72
 uses, 73
 Stearic acid, coffee, 157
 peppermint, 230
 water mint, 234
 Stearoptene, saffron, 281
 rose, 288
 Stem spices, **187**; *see also* Leaf spices
 Sterculia family, seed alkaloids,
 114
Sterculiceæ, 114
 Stermanis, 341
 Sterols, yeast, 485
Strychnos, 160
 Suage, 249
 Succinic acid, maple products, 41
 water mint, 234
 yeast, 489
 Sucrase, 510
 Sucrogenetic amylase, 43
 Sucrose, 1-3, 5-7, 9, 23
 coffee, 149, 160
 honey, 61
 maple products, 42
 paprika, 453
 sugar beet products, 33
 sugar cane products, 23
 Sugar, *see* individual saccharine
 products
 Sugar beet products, **29**
 composition, 30
 juice, 30

Sugar beet products,
 composition—(*Cont.*)
 massecuite, 31
 molasses, 31
 raw sugar, 30
 refined sugar, 31
 constituents, 32
 acids, 33, 34
 amino acids, 32
 carbohydrates, 33
 araban, 34
 invert sugar, 33
 pentosans, 33
 raffinose, 33
 sucrose, 33
 choline bases, 32
 colors, 34
 fuscazinic acid, 34
 mineral, 34, 35
 nitrates, 32
 proteins, 32
 manufacture, 29
 structure, 29

Sugar cane products, 10
 composition, 12
 cane, 13, 15, 24
 influence of climate, 13
 of stage of growth, 13
 juice, 14, 15
 massecuite, 15
 molasses, 15, 20
 hard, 21
 influence of soil, 21
 standards, 19, 21
 sirup, 15, 21
 standards, 21
 sugar, 15, 16
 brown, 17
 impurities, 17
 minor constituents, 18
 raw, 16
 standards, 17
 white, 17
 constituents, 21
 acids, 22
 amides, 22
 amino acids, 21
 anthocyanin, 23
 carbohydrates, 23
 dextrose, 23
 glucose, 23
 invert sugar, 23
 levulose, 23
 sucrose, 23

Sugar cane products,
 constituents—(*Cont.*)
 choline bases, 22
 colors, 23
 mineral, 23
 minor mineral, 18, 24
 copper, 24
 iron, 24
 manganese, 24
 proteins, 21
 purine bases, 22
 tannin, 23
 manufacture, 10
 refining, 12

Sugar, invert, sirup, *see* Invert sugar
 sirup

maple, *see* Maple products

palm sugar, 28
 date, 28
 nipa, 28
 palmyra, 28

sand, 36

sorghum, *see* Sorghum products

starch, *see* Starch sugar

Sugars, cardamom, 307
 black pepper, 335

Summer savory, 219, 221, 244
 composition, 245
 key, 221
 mineral constituents, 246
 oil, volatile, 245
 constituents, 245
 carvacrol, 245
 cymene, 246
 cymol, 246
 dipentene, 246
 pinene, 246
 values, 245
 pentosans, 246
 standards, 245
 structure, 244

Sweet basil, 219, 221
 composition, 222
 key, 221
 oil, volatile, 222
 constituents, 223
 d-camphor, 223
 cineol, 223
 linalool, 223
 methyl chavicol, 223
 ocimene, 223
 d- α -pinene, 223
 values, 222
 structure, 221

- Sweet birch, 258
 clover, 394
 corn, sugar, 27
 fennel, 429
 Sweet marjoram, 219, 221, **236**
 composition, 237
 key, 221
 mineral constituents, 239
 oil, volatile, 238
 constituents, 238
 carvacrol, 238
 terpinene, 238
 d- α -terpineol, 238
 terpineol-4, 238
 thymol, 238
 terpeneless, 239
 values, 238
 pentosans, 238
 standards, 238
 structure, 236
 Sweet orange, **399**
 oil, 399
 California, 400
 constituents, 401
 acetic acid, 401
 capric acid, 401
 caprylic acid, 401
 dl-carvone, 401
 citral, 401
 decyl alcohol, 401
 decyl aldehyde, 401
 formic acid, 401
 formaldehyde, 401
 d-linaloöl, 401
 d-limonene, 401
 methyl anthranilate, 401
 nonylic alcohol, 401
 octyl alcohol, 401
 d-terpineol, 401
 Florida, 401
 Sicilian, 399, 400
 Spanish, 400
 standards, 400
 Valencia, 399
 values, 399
 Washington Navel, 399, 400
 Sweet paprika, 443, 451, 455
 vernal grass, 394
 woodruff, 394
 Sylvestrene, 153
Symplocos caparoënsis, 90
 lanceolata, 90
 variabilis, 90
 Synadenylic acid, 497
- T**
- Taka-na, 377
 Tanacetone, 251
 Tangeretin, mandarin, 403
 tangerine, 403
 Tangerine, **403**
 oil, **403**
 constituents, 403
 tangeretin, 403
 values, 403
 Tannase, 108
 Tannic acid, 113
 Tannin, allspice, 413
 cocoa, 126
 coffee, 142, 153, 154
 cloves, 299
 honey, 59
 maté, 92
 nectar, 46
 spices, 183
 sugar cane, 23
 tea, 105, 107, 108
 Tannin-free coffee, 142, 153, 154
 Tannol, 157
Taraxacum Dens-leonis, 173
 officinale, 173
 taraxacum, 55
 Targone, 255
 Tarragon, **255**
 composition, 256
 oil, volatile, 256
 constituents, 257
 methyl chavicol, 257
 ocimene, 257
 phellandrene, 257
 terpeneless, 256
 values, 256
 structure, 255
 Tarragona, 255
 Tartaric acid, baking powder, 526
 cocoa, 133
 honey, 46
 nectar, 46
d-Tartaric acid, 526
 maple sand, 42
 maple sugar, 41
i-Tartaric acid, 526
l-Tartaric acid, 526
meso-Tartaric acid, 526
 Tartrate baking powder, 527
 Te, 94
 Té, 94
 del Paraguay, 87
 Tea, **94**
 adulteration, 95

Tea—(*Cont.*)

- black, 94, 100, 101, 105
- bohea, 94
- Ceylon, 95, 98, 101, 102, 106, 111
- Chinese, 94, 95, 98, 101-103, 106, 111
- composition, 97-101
 - influence of firing, 101
 - of maturity, 99
 - of method of curing, 100
 - of rolling, 100
- stems, 101
- Congo, 98, 111
- congou, 94
- constituents, 102
 - acids, 105
 - ascorbic, 105
 - oxalic, 105
 - tetramethyluric, 103
 - catechol, 107
 - colors, 109
 - carotene, 109
 - carotenoids, 109
 - quercetin, 109
 - xanthophyl, 109
 - enzymes, 109
 - catalase, 109
 - diastase, 109
 - oxidase, 109
 - peroxidase, 109
 - tannase, 108
 - mineral, 109, 110, 111
 - minor mineral, 111
 - aluminum, 111
 - fluorine, 111
 - iodine, 111
 - iron, 111
 - manganese, 111
 - odor, 109
 - oil, fixed, 103
 - acetic acid, 103
 - butyric acid, 103
 - caproic acid, 103
 - heptoic acid, 103
 - hexadecenoic acid, 103
 - o*-methoxybenzoic acid, 103
 - palmitic acid, 103
 - propionic acid, 103
 - valeric acid, 103
 - oil, volatile, 104
 - acetic acid, 104
 - acetone, 104
 - acetophenone, 105
 - alcohol, 104
 - benzaldehyde, 105
 - benzoic acid, 105

Tea,

constituents,

oil, volatile—(*Cont.*)

- benzyl alcohol, 104, 105
- benzyl-ethyl alcohol, 104
- butyraldehyde, 105
- butyric acid, 105
- caproaldehyde, 105
- caproic acid, 105
- caprylic acid, 105
- citral-*a*, 105
- citronellol, 105
- cresol, 104, 105
- geraniol, 104, 105
- hexanol, 105
- β , γ -hexanol, 104, 105
- β -hexen-1-ol, 104
- hexenal, 105
- α , β -hexenal, 104, 105
- hexenoic acid, 105
- hexoic acid, 104
- n*-hexyl alcohol, 104
- 4'-iododiphenylurethan, 104
- isobutyraldehyde, 105
- isovaleraldehyde, 104, 105
- isovaleric acid, 105
- linalool, 105
- methyl alcohol, 104
- methyl salicylate, 104, 105
- β -methyl-butan- α -ol, 104
- α -naphthylurethan, 104
- octanol, 105
- n*-octyl alcohol, 104
- oxytheotannin, 109
- palmitic acid, 105
- phenethyl alcohol, 104, 105
- phenol, 104
- phenylacetic acid, 105
- phenylethanol, 105
- propionic acid, 105
- proteins, 102
- purine bases, 102
 - caffeine, 102
 - guanine, 103
 - tetramethyluric acid, 103
- quinoline, 105
- salicylic acid, 104, 105
- saponin, 108
- tannin, 105-108
- theotannin, 106
- facing, 95
- flowery pekoe, 94
- Formosan, 105, 107
- grades, 94
- green, 94, 98, 100, 101, 104, 108, 109

Tea—(Cont.)

- gunpowder, 94
- hyson, 94
- Indian, 95, 98, 101, 102, 106
- Isola madre, 102
- Japan, 95, 102, 110, 111
- Java, 98, 101, 110
- Java-Pecco, 102
- Kongo, 111
- oolong, 98, 110, 111
- orange pekoe, 94
- Pavia, 102
- pekoe, 94
- rolled, 101
- souchong, 94
- stems, 101
- structure, 95, 96
- Tea family, alkaloidals, 94
- Tee, 94
- Ternstræmiaceæ*, 94
- Terpenes, celery, 440
 - Ceylon cinnamon, 275, 276
 - coffee, 153
 - nutmeg, 355
 - Ocimum gratissimum*, 224
 - Papua Massoi oil, 269
 - rose, 289
 - spices, 181, 185
- Terpinene, cardamom, 307
 - dill, 426
 - marjoram, 221
 - peppermint, 229
 - sweet marjoram, 238
- α -Terpinene, coriander, 419
 - Ocimum viride*, 223
- γ -Terpinene, coriander, 419
 - lemon, 405
 - Ocimum viride*, 223
- Terpineol, bay leaf, 218
 - bergamot, 402
 - juniper berry, 302
 - lemon, 405
 - marjoram, 221
- α -Terpineol, nutmeg, 355
 - orange flower, 402
 - star anise, 343
- d*-Terpineol, nutmeg, 355
 - orange, 401
- d*- α -terpineol, cardamom, 307
 - sweet marjoram, 238
- i*-Terpineol, 355
- l*- α -Terpineol, 218
- Terpineol-4, sweet marjoram, 238
 - thyme, 242
- Terpinol, 185
- Terpinolene, 420
- Terpinyl acetate, 307
- Tetrahydroxycyclohexane, 160
- Tetramethyltrioxypurine, 84
- Tetramethyluric acid, alkaloidal products, 82, 84
 - tea, 103
- Tetraphosphoric acid, 497
- Thé, 94
- Thea assamica*, 94
 - bohea*, 94
 - lasiocalyx*, 94
 - sinensis*, 94
 - stricta*, 94
 - viridis*, 94
- Theobroma Cacao*, 114
- Theobromase, 126
- Theobromine, alkaloidal products, 81-83
 - cocoa, 126, 128
 - cola nut, 138
- Theophylline, alkaloidal products, 82, 84
- Theotannin, 106
- Thiamin, xx, xxi
 - yeast, 501, 502, 520
- Thiochrome, 502
- Thiocyanates, 182
- Thuja*, 251
- Thujone, 221, 251
- Thym, 240
- Thyme, 219, 221, 240
 - composition, 240
 - key, 221
 - oil, volatile, 241
 - constituents, 242
 - borneol, 242
 - l*-borneol, 242
 - camphene, 242
 - camphor, 242
 - carvacrol, 242
 - citral, 242
 - cymol, 242
 - geraniol, 242
 - linaloöl, 242
 - l*-linaloöl, 242
 - menthene, 242
 - β -pinene, 242
 - l*-pinene, 242
 - terpineol-4, 242
 - thymol, 242
 - values, 241
 - pentosans, 243
 - standards, 241
 - structure, 240

Thymian, 240
 Thymol, 182
 Ocimum viride, 223
 Origanum virens, 239
 Satureia Thymba, 246
 sweet marjoram, 238
 thyme, 221, 242
 Thymus marschallianus, 243
Thymus capitatus, oil, 243
 marschallianus, oil, 243
 odoratissimus, oil, 243
 Serpyllum, oil, 243
 striatus, oil, 243
 vulgaris, 240
 Timo, 240
 Tobasco allspice, 408
 α -Tocopherol, xxvi, xxvii
 β -Tocopherol allophanate, xxvii
 γ -Tocopherol allophanate, xxvii
 Tomillo, 240
 Tonka bean, 309, 314, 389, **394**
 butter, 396
 composition, 396
 coumarin, 396
 extract, 314, 396
 fat, 396
 structure, 394
 Tonkabohne, 394
 Tonquin bean, 394
 Tori, 367
 Toxisterol, xxv
 Trehalose, 492
 Tricarballic acid, maple sand, 42
 maple sugar, 41
 Tricontane, 259
 Tridecylic acid, 197
Trigonella Fænum-Græcum, 389
 Trigonelle, 389
 Trigonelline, 155
 Trimethyl amine, coffee, 148
 water mint, 234
 yeast, 483
 Trimethylamine oxide, 32
 Trimyristin, 353
 Triolein, 353
 Triose monophosphate, 495
 Triosemonophosphoric acid, 495
 Tripalmitin, 353
Tritonia aurea, 278
Tropæoluccæ, 398
Tropæolum majus, 283, 398
 minus, 398
 α -Truxilline, 86
 Truxillococaine, 86
 Trypsin, 506

Tryptase, 505
 Turmeric, **211**
 carbohydrates, 214
 color, 214
 composition, 212
 curcumin, 214
 long, 211
 oil, fixed, 213
 oil, volatile, 213
 constituents, 213
 d-camphene, 213
 d-camphor, 213
 cineol, 213
 l-curcumene, 213
 curcumone, 213
 phellandrene, 213
 d- α -phellandrene, 213
 turmerol, 213
 values, 213
 pentosans, 214
 round, 211
 structure, 211
 Turmerol, 213
 Tyrosine, beet molasses, 32
 sugar cane products, 22

U

Umbelliferae, 414
Umbellularia californica, 217
 Undecylic acid, orris, 197
 Thymus marschallianus, 243

V

Vacuum-packed coffee, 142, 150
 Vainiglia, 308
 Vainilla, 308
 Valeraldehyde, 491
 Valerianic acid, 158
 Valeric acid, bay leaf, 218
 chicory root, 172
 honey, 60
 tea, 103
Vangueria madagascariensis, 139
 Vanilla, **308**
 Bourbon, 308, 311, 312, 314, 316
 Central American, 310
 Ceylon, 308, 312, 314
 Comores, 312, 314
 composition, 312
 constituents, 316
 glucovanillic alcohol, 317

- Vanilla,
 constituents—(*Cont.*)
 glucovanillin, 317
 heliotropin, 318
 isovanillin, 317
 methyleneprotocatechuic acid, 317
 methyleneprotocatechuic aldehyde, 318
 methylprotocatechuic aldehyde, 316
 mineral, 318
 pentosans, 318
 piperonal, 318
 resins, 318
 vanillic acid, 317
 vanillin, 316
 extract, 308, 312
 composition, 313, 314, 316
 menstrua, 315
 standards, 308
 Fiji, 308
 Java, 308, 312, 314
 Madagascar, 308, 312, 314
 Mexican, 308, 310, 312, 314, 316
 Réunion, 308
 Seychelles, 308, 312, 314
 South American, 308, 312, 314
 standards, 308
 structure, 309
 Tahiti, 308, 312, 314-316
 Vanilla grass, 394
Vanilla planifolia, 308
 Vanille, 308
 Vanillic acid, maple products, 42
 vanilla, 317
 Vanillin, 182, 184, 316
 cloves, 298
 maple products, 42
 preparation, 317
 sugar, 309
 synthetic, 308
 vanilla, 316
 Vanillone, 153
 Vanillons, 312, 314
 Vanirom, 309
 Veilchen, 290
 Veilchenwurzel, 196
 Vigantol, xxv
p-Vinyl catechol, 153
 Vinyl guaiacol, 152
p-Vinyl guaiacol, 153
Viola, 290
Violaceæ, 290
 Violet, 290
 oil, 290
 constituents, 290
 values, 290
 Violet family, flower spice, 290
 Violeta, 290
 Violetta, 290
 Violette, 290
 Vitamin A, xix
 Vitamin A₁, xx
 Vitamin A₂, xx
 Vitamin B, xx, xxx
 Vitamin B₂, xxvii
 yeast, 501, 505
 Vitamin B₆, xxi, xxii, xxix, xxx
 Vitamin C, xxii, xxx
 Vitamin D, xxiii, xxv; *see also* Calci-ferol
 Vitamin D₂, xxv
 Vitamin D₃, xxiv, xxv
 Vitamin D₄, xxv
 Vitamin E, xxvi
 Vitamin G, xxvii
 yeast, 501, 505
 Vitamin H, xxx
 Vitamin K, xxx
 Vitamin L, xxx
 Vitamin L₁, xxx
 Vitamin L₂, xxx
 Vitamin P, *see* Citrin
 Vitamins, xix
 fish, xx
 mammals, xx
 oranges, xxxi
 yeast, 520

W

- Wacholderbeere, 301
 Waldmeister, 394
 Warburg's enzyme, 519
 Wassermanze, 233
 Water mint, 219, 221, 231, **233**, 235
 ammonium chloride, 234
 aquaticol, 234
 betaine, 234
 butyric acid, 234
 choline, 234
 dextrose, 234
 dotriacontane, 234
 formic acid, 234
 heptylic acid, 234
 hexylic acid, 234
 linaloöl, 234

Water mint—(*Cont.*)

- linolenic acid, 234
- linolic acid, 234
- melissic acid, 234
- methylamine, 234
- myristic acid, 234
- oil, 233
 - constituents, 234
 - acetic acid, 234
 - aldehyde, 234
 - furfural, 234
 - linalool, 234
 - linalool acetate, 221, 231, 234
 - lupeol, 234
 - phytosterol, 234
 - sesquiterpenes, 234
 - trimethylamine, 234
 - values, 233, 234
- oleic acid, 234
- palmitic acid, 234
- potassium nitrate, 234
- rhamnose, 234
- stearic acid, 234
- succinic acid, 234

Wax, coffee, 157

grapefruit, 407

Weisser Senf, 378

Wheat, 150, 151

White mustard, 361, 362, 368, 369, 371.
378

California, 363, 381, 383

Cambridge, 381, 384

carbohydrates, 383

pentosans, 383

composition, 380, 381

Dutch, 381, 383

English, 381, 383

enzymes, 383

myrosin, 382

phosphatase, 371

flour, 381

German, 381, 383

mineral constituents, 383

oil, fixed, 380

values, 380

oil, volatile, 381

sinalbin, 382

sinigrin, 381

parahydroxybenzyl isothiocyanate,
382

phosphorus-organic compounds, 383

phytin, 383

proteins, 380

globulin, 380

sinalbin mustard oil, 382

White mustard—(*Cont.*)

sinapin, 383

sinapinic acid, 383

structure, 378

Yorkshire, 381, 384

White sugar, *see* Sugar cane products

Wild caraway, 437

cardamom, 303, 306

clary, 253

coffee, 140, 155

mint, 231

pulegone, 231

Willia javanica, 514

Winter savory, 244, 246

oil, constituents, 246

values, 246

Wintergreen, 258

extract, 259

standards, 259

oil, 259

methyl salicylate, 259

oenanthaldehyde, 259

tricontane, 259

values, 259

Woodruff, sweet, 394

X

Xanthine, alkaloidal products, 82

Xanthophyl, capsicums, 460

chillies, 460

nutmeg, 356

paprika, 454

tea, 109

Xylan, 133

Xylose, 133

Y

Yeast, 465

baker's, xxx

composition, 478

influence on bread, 479

constituents, *see* Yeast constituents

manufacture, 466

Hayduck process, 466

Vienna process, 466

meat substitute, 469

nitrogenous foods, 467

nutritive value of, 469

relation to mushrooms, 470

storage, 468

structure, 477

forms, 477

staining, 478

Yeast constituents, 479

acids, 487

acetic, 487

acetylcarboxylic, 487

aldehyde, 492

butyric, 487, 489

formic, 487

lactic, 487, 489

nicotinic, 490

nucleic, 490, 498

propionic, 487

pyroracemic, 487

pyrouvic, 487

pyruvic, 487

succinic, 489

alcohols, 490

amyl, 490

butanol, 490

butyl, 490

ethanol, 490

ethyl, 490

glycerol, 491

methanol, 490

methyl, 490

saligenin, 491

aldehydes, 491

acetaldehyde, 491

acetic, 491

aromatic, 492

cinnamaldehyde, 492

cyclic, 492

decaldehyde, 492

dialdehydes, 492

ethyl, 491

formaldehyde, 492

hydroxyaldehyde, 492

ketoaldehyde, 492

valeraldehyde, 491

amines, 483

amylamine, 483

trimethylamine, 483

amino acids, free, 483

of yeast proteins, 480

bioses, 521

carbohydrates, 492

achroocellulose, 494, 495

cellulose, 494

dextran, 494

erythrocellulose, 494, 495, 513

gentiobiose, 492

glycogen, 492

hemicellulose, 494

mannan, 493

mannodextran, 494

mannose, 510

Yeast constituents,

carbohydrates—(Cont.)

polysaccharides, 495

trehalose, 492

yeast cellulose, 494

yeast gum, 493, 510

chitin, 483

chloral hydrate, 492

choline bases, 483

choline, 483

coenzymes, 505; *see also* enzymes

colors, 501

coproporphyrin, 503

cytochrome, 503

etioporphyrin, 504

flavin, 501

hematin, 502

hematoporphyrin, 503

hemin, 502

hemochromogen, 502

hemoglobin, 503

iron porphyratin, 502

porphyrin, 503

riboflavin, 504

thiochrome, 502

enzymes, 505

alcohol-dehydrogenase, 517

aldehyde-mutase, 518

aldehydease, 510

aminopolypeptidase, 506

amygdalase, 513

amylase, 512

amylopectinase, 513

amylosynthase, 513

anti-invertase, 512

asparaginase, 506

carboligase, 510

carboxylase, 507

catalase, 505

cellobiase, 514

cocarboxylase, 507

codehydrogenase, 509

coreductase, 508

cozymase, 515

dehydrase, 508

dehydrogenase, 508

dipeptidase, 506

emulsin, 513

endotryptase, 507, 515

erepsin, 506

ereptase, 505

galactase, 518

glucase, 518

glucosidase, 513

glycophosphatase, 518

Yeast constituents,

enzymes—(*Cont.*)

hexosediphosphatase, 519

inulase, 513

invertase, 510

lipase, 507

maltase, 512

methyl glyoxalase, 518

oxidation enzymes, 519

pepsin, 505

peptidase, 505

phosphatase, 518

phytase, 520

polypeptidase, 506

protease, 505

proteinase, 505, 506

pyrophosphatase, 519

reductase, 507, 508, 518

saccharophosphatase, 518, 519

sucrase, 510

trypsin, 506

tryptase, 505

Warburg's 519

zymase, 507, 514, 518

fat, 483

composition, 484

gum, 493, 510

hormones, 520

insulin, 520

hydrocyanic acid, 483

mineral, 522

minor mineral, 523

aluminum, 523

argon, 524

arsenic, 524

copper, 524

iodine, 524

iron, 523

manganese, 523

zinc, 524

phosphorus-organic compounds, 495

adenosine triphosphate, 497

adenosinetriphosphoric acid, 497

adenylic acid, 496

cephalin, 497, 498

hexose diphosphate, 495

hexosediphosphoric acid, 495

hexose monophosphate, 495, 496

hexosemonophosphoric acid, 496

inosine pyrophosphate, 497

inosinepyrophosphoric acid, 497

lecithin, 497

nucleic acid, 498

phosphodihydroxyacetone, 495

Yeast constituents,

phosphorus-organic compounds—

(*Cont.*)

phosphoglyceraldehyde, 495

2-phosphoglyceric acid, 495

3-phosphoglyceric acid, 495

 α -phosphoglycerol, 495

phosphopyruvic acid, 495

triose monophosphate, 495

triosemonophosphoric acid, 495

proteins, 479

amino acids, 480

cerevisin, 479, 480

fungus mucin, 480

nitrogen distribution, 482

zymocasein, 479, 480

purine bases, 483

xymin, 483

pyrimidine bases, 483

sterols, 485

anasterol, 487

ascosterol, 486

cerevisterol, 487

cryptosterol, 486, 487

 α -dihydroergosterol, 487

episterol, 487

ergosterol, 485, 487

fecosterol, 486

hyposterol, 487

neosterol, 486

squalene, 486

zymosterol, 486

sulphur-organic compounds, 500

adenyl thiopentose, 500

glutathione, 500

thiamin, 501

vitamin B, 501, 502, 520

vitamins, 520

A (added carotene), 520

B (thiamin), 501, 502, 520

D (by irradiation), 520

G (riboflavin), 501, 505, 520

L, xxx

Z

Zafferano, 278

Zea Mays, 1

Zeaxanthin, 454

Zedoary, 198, 211

round, 198, 211, 213

Zenzero, 198

Zimtblüten, 357

Zimtkassie, 261

- Zinc, 524
Zingerone, 207
Zingiber, 198
 Cassumunar, 199
 Mioga, 198
 officinale, 198
 Zerumbet, 198
Zingiberaceæ, 198, 303
- Zingiberene, 182
 ginger, 209, 210
Zingiberol, 182
 ginger, 209, 210
Zingiberone, 207
Zymase, yeast, 507, 514, 518
Zymogen, 513
Zymosterol, 486



AM
8/8/89
2949

CHECKED
2008
Am

VERIFIED
2013
Alc

CFTRI-MYSORE



705

Structure and co

Acc. No. 705

3;e N35.4

TON (AL).

re and

Food

